GOLD IN SEA WATER

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GOLD IN SEA WATER

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ABSTRACT

The geochemistry of gold in the marine environment was studied to determine possible natural concentrating processes which may be used to extract gold. Radioactive gold tracers ^{195}Au and ^{198}Au were used in the investigations. The solubility of gold in sea water was determined to be on the order of 4 µg Au/l, in the same order of magnitude as predicted by Sillén. The distribution of gold in equilibrated solutions originally saturated was variable when the solution was agitated. Reproducible values were obtained when the solution was centrifuged.

Differences in the ion exchange properties of gold +1 and gold +3 were determined by experiments with electrolytically produced mixed solutions of auric and aurous chloride which were passed through strong anion exchange columns. Approximately 10% of the soluble gold in equilibrated sea water solutions was non-ionic. The soluble character of the gold in these solutions was unchanged when mixed with sulfide waters. This indicates that gold would not be concentrated in anoxic basins. The character of soluble gold was also studied using dialysis and electrophoresis.

Soluble gold was rapidly adsorbed on several clays followed by a release of gold within about 24 hrs of the mixing time. This is about the time observed by Lingane for the equilibrium shift of auric to aurous gold.

$$Au\,Cl_4^- + 2\,Au + 2\,Cl^- \rightleftharpoons 3\,Au\,Cl_2^- \qquad K_{eq} = 1.8 \times 10^{-8}$$

Gold is easily reduced and adsorbs on many different materials. Most materials used in sampling and analysis for gold in aqueous media

adsorbed gold least from acidified solutions. Rubber and cellulose ester fiber filters were notable exceptions.

Neutron activation methods have been devised to analyze marine samples for gold. Analyses of samples from southeast Alaska indicate that gold in sea water is predominantly in a soluble non-ionic form, with ionic and particulate forms making up only about 20% of the total.

The average gold content in these waters is 3 ng Au/l with a range of 1 to 11 ng Au/l. Analyses of sediment in Gold Creek and Gastineau Channel at Juneau, Alaska indicate that the transport of gold is mainly by physical means with the majority of the gold appearing in the 4 ϕ size range in and near Gold Creek.

Cationic forms of gold in sea water are nil and gold is not associated to any great extent with dissolved organic matter which is extractable in either chloroform or ethyl acetate.

The gold concentrations in samples from the east Pacific indicate a heterogeneous distribution. The average concentration was 4 ng Au/l with a range of 1 - 25 ng Au/l.

Approximately 10% of the gold in sea water is ionic, probably gold +1 chlorohydroxy anions, e.g., $AuClOH^-$. Another 10% is associated with particulate matter and the remaining 80% is less than 0.45 μ, non-ionic, not extractable in ethyl acetate nor chloroform, and probably colloidal.

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GOLD IN THE MARINE ENVIRONMENT

INTRODUCTION

The presence of gold in sea water has been known for nearly two hundred years, with numerous values being reported in the later half of the nineteenth century. These values ranged from 2-64 µg Au/l. A good account of this early work was reported by Stark (1943). Man's desire for this precious metal prompted many to attempt economical removal of gold from sea water. A list of patents for gold extraction is given by Haber (1927). One such venture developed into a classic in analytical chemistry and served to quell much of the effort being made to extract gold from the oceans.

The work of Fritz Haber (1927, 1928) began in 1918, and was an attempt to pay Germany's war debt with gold from the oceans. He and his co-workers made some 4,500 analyses of samples from various parts of the world. He started by analyzing water from river estuaries and found that the gold content increased with the salt content.

Haber's (1927) method of analysis was to add lead acetate and ammonium sulfide to fresh sea water samples. The gold was precipitated with the lead sulfide, separated from solution, and treated with lead formate and boric acid. Then the gold content was determined by fire assay. The resulting gold bead was measured with the aid of a microscope. As his method was improved, the concentrations of gold in sea water decreased. Haber (1927) reported an average value of 0.01 µg Au/l in North Atlantic water and later (1928) 0.004 µg Au/l for South Atlantic water, an average of approximately 1,390 analyses. The range of values was 0.001 - 0.059 µg Au/l. Haber (1928) found generally higher values

for surface water and was able to substantially decrease the gold content by centrifuging the sample prior to analysis which lead him to conclude that gold was associated with particulate matter. He also found that gold values in replicate samples varied more than could be accounted for by the error in his method. He attributed this to "clumping" as might result from gold associated with particulate matter. Even though Haber (1927, 1928) found an occasional high gold value, he concluded that the average content of gold in the oceans, 0.004 µg Au/l, was far too low to be economically extracted. A co-worker, Jaenicke (1935), reported that Haber was convinced gold could not be economically extracted from sea water, but continued his work as a contribution to science.

Subsequent analyses of sea water for gold by other investigators (Table 1) have tended to confirm Haber's findings. Caldwell (1938) set an upper limit for gold concentrations in Puget Sound water, 0.2 µg Au/l. He felt there was a strong tendency for gold to be removed from water by organic matter.

Stark (1943) used charcoal to adsorb gold from sea water in the Mediterranean Sea and Atlantic Ocean off Spain. His values ranged from 0.009 to 2.0 µg Au/l, the highest in the Atlantic water.

Putnam (1953) analyzed sea water from both the east and west coasts of the United States. He found that the gold concentration in the east coast waters was below his limit of detection, 0.05 µg Au/l. His highest values were from a Puget Sound estuary and averaged 44 µg Au/l. Putnam (1953) found (as had Caldwell, 1938) that the water in the sea water storage tanks at the University of Washington was very low in gold,

Table 1. Some Reported Values of Gold

Approx. Conc. µg/l	Method of Separation
0.004	Co-pptn. with PbS, treated with lead formate and H_3BO_3
0.1 - 0.2	Co-pptn. with colloidal Hg/HgCl
0.02 - 2.0	Adsorbed on charcoal
0.003 - 44	Co-pptn. with Na_2S and $FeCl_3$ ppt dissolved, Co-pptn. with HgS
0.01 - 0.5	Neutron activation, ethyl acetate extraction from HCl solution, pptd.
0.009	Anion exchange concentration Au recovered from ashed resin
0.068 $\pm$ 0.003	Co-pptn. with 2-mercaptobenimidazole, wet ashed, co-pptn. with Te using Sn^{2+}
0.0056	Sample freeze dried, neutron activation. Au pptd. with carrier
0.010 - 0.013	Solvent extraction

Concentration in Sea Water

Method of Determination	Reference
Fire assay, micrometry of bead	Haber, 1928
Fire assay	Caldwell, 1938
Fire assay	Stark, 1943
Photometric	Putnam, 1953
Counting of gold-198	Hummel, 1957
Spectrographic	Brooks, 1960
Photometric	Weiss and Lai, 1963
γ-spectrometry	Schutz and Turekian, 1963
Atomic absorption spectroscope	Rosenbaum, May and Riley, 1969

perhaps removed by the organic matter which accumulated in the bottom of the tanks.

Hummel (1957) was the first to use neutron activation analysis for gold in sea water. He used stringent procedures to control contamination and sorption. Quartz ampules were used to store and irradiate 4-6 ml samples. He found gold concentrations decreased with distance from shore and attributed this to association of gold with particulate matter.

A strong anion exchange resin was used by Brooks (1960) to obtain an enrichment factor of 2×10^7 prior to spectrographic analysis. His method was to oxidize the gold with bromine added to acidified sea water prior to running the solution through the ion exchange resin.

Co-precipitation with a 2-mercaptobenzimidazole was used by Weiss and Lai (1963) to extract gold from large volumes (ca 30 1) of sea water. They used a radioactive tracer, ^{195}Au, to test their method. A basic assumption was that gold in acidified sea water was in the same chemical form as the radioactive gold added, $AuCl_4^-$.

Schutz and Turekian (1965) used neutron activation analysis to determine gold and a number of other elements in 100 ml samples of sea water. The samples were concentrated by freeze drying prior to irradiation. Their values were in the same range as those found by Hummel and Haber, but with greatly improved reproducibility.

Rosenbaum et al. (1969) employed solvent extraction to remove gold from sea water. They used bromine and hydrobromic acid to oxidize the gold prior to extraction. The $AuBr_4^-$ complex exhibits better extraction characteristics than the $AuCl_4^-$ complex (Cornish, 1960). Rosenbaum et al. (1969) investigated anion-exchange resin as a concentration proce-

dure, but abandoned it because of the time required to process large quantities of sea water. They calculated the value of gold in sea water and the cost of extraction, further demonstrating the unfeasibility of gold extraction from sea water with presently known methods.

Numerous other methods are available for concentrating gold from water and its ultimate analysis. Mercury (Jenne et al., 1968) and cyanide (Burstall et al., 1953) have both been used for years in the gold mining industry. Carbon paste electrodes have been used with anoidic stripping voltammetry (Jacobs, 1963), but this technique has a lower limit of detection of 1 μg Au/l and poor electrode reproducibility. A summary of electroanalytical methods is given by Beamish (1969). Beamish (1961) also reviewed colorimetric and spectrographic methods for gold analysis. A comparison of various methods of analysis for a number of trace elements is given by Hume (1967), indicating neutron activation analysis is the most sensitive for gold. Neutron activation analysis of gold in ores was compared with wet assay and fire assay by Chow and Beamish (1967), and a critical review of neutron activation methods for noble metals was presented by Beamish, Chung and Chow (1967). Mizuike et al. (1965) used ion exchange concentrations and neutron activation analysis to determine gold in copper metal. Extensive characterization of the strong anion exchange resin, Dowex-1 (Amberlite IRA-400 or BIO-RAD AG-1) was reported by Kraus and Nelson (1954).

A chelating resin, SRXL, reported by Koster and Schmuckler (1967) has been found to be highly selective for noble metals. Green and Law (1970) used the resin to extract gold from solutions of geological material. Bayer (1964) also developed a gold specific ion exchange resin

which has been used to extract gold from sea water (Zlatkis et al., 1969).

An enormous amount of work has been done on the analysis of gold in geological materials. The early work was done almost exclusively by fire assay. Atomic absorption spectroscopy, AAS, is now quite popular for analysis of ore quality geological materials (Tindall, 1965; Clifton et al., 1967; Huffman et al., 1967; Van Sickle and Lakin, 1968).

OXIDATION STATES OF GOLD

Gold, atomic number 79, is 100 percent ^{197}Au with an atomic weight of 196.967. The electron configuration is [Xe] $4f^{14}$ $5d^{10}$ $6s^{1}$ with the first three ionization potentials 9.23, 20.1, and 30.5 eV, respectively (Cotton and Wilkinson, 1966).

The most common oxidized states are gold (I) and gold (III). The amount of free ion in solution is very small as shown by equilibrium data for gold (I) by Sillén (1961) and Goolsby and Sawyer (1968),

$$AuCl_2^- \rightleftharpoons Au^+ + 2\ Cl^- \qquad K = 10^{-20} \qquad (1\text{-}1)$$

and for gold (III) by Latimer (1952),

$$AuCl_4^- \rightleftharpoons Au^{+3} + 4\ Cl^- \qquad K = 5 \times 10^{-22} \qquad (1\text{-}2)$$

and

$$Au(OH)_4 \rightleftharpoons Au^{+3} + 4\ OH^- \qquad K = 8.5 \times 10^{-45} \qquad (1\text{-}3)$$

The oxidation potentials determined by Lingane (1962) are:

$$Au + 2Cl^- \rightleftharpoons AuCl_2^- + e^- \qquad E = -1.154V \qquad (1\text{-}4)$$

$$AuCl_2^- + 2Cl^- \rightleftharpoons AuCl_4^- + 2e^- \qquad E = -0.926V \qquad (1\text{-}5)$$

$$Au + 4Cl^- \rightleftharpoons AuCl_4^- + 3e \qquad E = -1.002V \qquad (1\text{-}6)$$

The relationship between gold (I) and gold (III) in chloride solutions is given by Lingane (1962)

$$AuCl_4^- + 2Au + 2Cl^- \rightleftharpoons 3AuCl_2^- \qquad K = 1.8 \times 10^{-8} \qquad (1\text{-}7)$$

Gold (III) may be present in sea water to a greater extent than indicated by the equilibrium data as gold (III) forms more stable organometal complexes than gold (I) (Remy, 1956; Emery and Leddicott, 1961). Gold (III) has a coordination number of 4 and usually forms square-planar complexes (Cattalini et al., 1967).

Gold (II) compounds have been proposed, e.g., gold sulfide, but this is probably a mixture of Au_2S and Au_2S_3 (Remy, 1956).

In the laboratory, gold is usually put into solution by heating with aqua regia ($HCl:HNO_3$ = 3:1) to produce $AuCl_4^-$. Auric chloride can also be produced by boiling gold in dilute hydrochloric acid enriched with hydrogen peroxide (Longerich, 1967). A mixture of $AuCl_2^-$ and $AuCl_4^-$ can be produced by anodization of a gold electrode in dilute hydrochloric acid (Lingane, 1958; Longerich, 1967).

THE SOLUBILITY OF GOLD IN SEA WATER

The presence of gold in sea water has been demonstrated by several investigators. While gold is considered inert to dissolution in most media, its solution time in sea water is finite. Putnam (1953) dissolved

gold film in sea water enriched with ozone in a matter of hours. Rosenbaum et al. (1969) used gold containing radioactive ^{195}Au to show a solubility of gold in sea water to be over three orders of magnitude greater than that normally found in the ocean.

Sillén (1961) used equilibrium constants published by Bjerrum (1948) to calculate the solubility of gold in sea water. He calculated a value for $AuCl_2^-$ of 12.6 µg Au/l and gold (III) species of ca. 0.008 µg Au/l. This calculated solubility of gold in sea water is about a thousand times higher than most of the values reported. Sillén (1961) concluded that metallic gold would be unstable in contact with sea water.

There are several explanations for the apparent undersaturation of gold in sea water. Manskaya and Drozdova (1968) report gold associated with porphyritic feldspar and in graphite tuff. The latter may represent biogenetic deposition. Gold is also found concentrated in shales to ca. 1 g/t. They also suggest that gold should be precipitated in a sulfide media. Rankama and Sahama (1950) suggest that gold is transported as a colloid and precipitated from sea water by adsorption on hydrolyzate sediments.

Some enrichment of gold was noted in a manganese nodule by Goldschmidt and Peters (according to Rankama and Sahama, 1950), however, Crocket et al. (1968) report no significant difference between the gold content in manganese nodules and marine sediments, 2-3 µg/g.

FORMS OF GOLD IN SEA WATER

Ionic gold exists most commonly as the anion of either gold (I) or

gold (III). Of the anions available in sea water for complexing, chloride is the most abundant with hydroxyl and bromide ions to a lesser extent. However, gold hydroxides are favored in the slightly basic sea water (pH = 7.8-8.2) as shown by Sillén's (1961) calculations. The ratio of $Au(OH)_4^-$:$AuCl_4^-$ is about 630. His conclusion that $AuCl_2^-$ would be the dominant gold ionic species in sea water is probably because the equilibrium constants for the formation of gold (I) chlorohydroxy complexes are not available.

$$AuCl_2^- + OH^- \rightleftharpoons AuClOH^- + Cl^- \qquad K_1 = (?) \qquad (1\text{-}8)$$

$$AuClOH^- + OH^- \rightleftharpoons Au(OH)_2^- + Cl^- \qquad K_2 = (?) \qquad (1\text{-}9)$$

Using the equilibrium constants for gold (III) chlorohydroxy complexes published by Bjerrum (1948) the following relationships between the complexes were calculated:

$AuCl_4^-$	0.01%
$AuCl_3OH^-$	1.6
$AuCl_2(OH)_2$	28.9
$AuCl(OH)_3$	43.9
$Au(OH)_4^-$	25.6

By analogy the dominant gold (I) species would probably be $AuClOH^-$ or even $Au(OH)_2^-$ rather than $AuCl_2^-$.

From equation 1-7 it can be seen that it is impossible to maintain pure solutions of aurous chloride; this has seriously interferred with attempts to measure gold (I) chlorohydroxy complex equilibrium constants.

The metallic gold formed as the reaction proceeds to the left would undoubtedly be colloidal in dilute solutions.

The determination of the aurous equilibrium constants may also be complicated by the reaction

$$AuCl_2^- + OH^- \rightleftharpoons AuOH + 2Cl^- \qquad (1\text{-}10)$$

(Remy, 1956). The gold hydroxide is probably present in sea water as a colloid.

Colloidal gold is well known and its stability in electrolytic systems is believed to be aided by protective colloids such as silica (Krauskopf, 1967).

Haber (1928) was able to reduce the amount of gold in sea water samples by centrifuging them, and Hummel (1957) found decreasing amounts of gold with distance from shore. Both were convinced that gold was associated with particulate matter.

Recent work (Morgan, 1968) in studies of organic matter in sea water and its association with metals indicates that some of the gold may be in the form of metal-organo complexes. Also, as suggested by Mason (1966), certain non-ionic substances (organics) may provide a protective coating for colloids.

Little is known of the biological role of gold. High gold content in plants usually reflects gold content in the soil. Fukai and Meinke (1959) report gold enrichment in sea weed and soft parts of fish. Bowen (1968) found gold enriched in marine sponges.

SUMMARY

As man continues to search for sources of the precious metals, gold included, he turns time and again to the oceans. Even though it is well established that gold cannot be economically extracted directly from sea water at this time, it may well be that there are natural concentration processes which can be used for this purpose. In order to take advantage of possible natural concentration processes we need a far better understanding of the complex character of gold in sea water. Unknowns pertaining to gold in sea water such as solubility, ionic character, particulate matter associations, and association with organic matter need to be investigated. Analytical methods need to be worked out to determine fractions of the total amount of gold in sea water, e.g., particulate versus soluble. Of special interest is the distribution and character of gold in the open ocean, marine sediments, and coastal areas, especially near known terrestrial gold deposits. It is the intent of this thesis to improve insight into the geochemistry of gold in the marine environment, using the most modern techniques.

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CHAPTER II

THE ANALYSIS OF SEA WATER FOR GOLD IN ITS VARIOUS FORMS

INTRODUCTION

Sea water has been analyzed for gold by a number of investigators (Chapter I), but most of them analyzed for total gold with few attempting to delineate the character of the gold. Gold associated with particulate matter has been suggested by Haber (1928) and Hummel (1957). Ionic gold has been predicted by Sillén (1961) and colloidal gold by Haber (1927) and Garrels and Christ (1965). Non-ionic complexes, both organic and inorganic, have been proposed (Remy, 1956). Doubt remains as to the form or forms and association of gold in sea water. It is the intent of this research to characterize gold in sea water through laboratory experiments using radioactive tracers and to devise analytical procedures necessary to determine gold in its various possible forms in the oceans. This study is concerned with the amount of gold in sea water as suspended particulate matter, as colloidal, and in solution in ionic, non-ionic organic and non-ionic inorganic forms.

TRACER STUDIES

The problems associated with sampling the marine system were investigated in the laboratory using specially prepared sea water containing radioactive gold tracers. Two readily available tracers used in the experiments are characterized in Table 2-1. Two basic assumptions made in the use of radioactive tracers are: 1) that stable and radioactive isotopes have identical chemistry and, 2) that the chemical form of the element of interest and its tracer are the same. The first assumption is well accepted, however the latter premise can create problems espe-

Table 2-1

Radioactive Gold Isotopes Used in Tracer Work

Isotope	$^{195}_{79}Au$	$^{198}_{79}Au$
Half-life, t 1/2	183d	2.7d
Method of Production	$^{195}_{78}Pt(p,n)\ ^{195}_{79}Au$	$^{197}_{79}Au(n,\gamma)\ ^{198}_{79}Au$
Decay	$^{195}_{79}Au(EC,\gamma)\ ^{195}_{78}Pt$	$^{198}_{79}Au(e^-,\gamma)\ ^{198}_{80}Hg$
Irradiation Measured	99 keV (10%)	412 keV (95%)
Obtained From:	Nuclear Science Division International Chemical & Nuclear Corporation Pittsburgh, Pa. 15236 Batch No. 8, Ref. Date - 8-20-68	Produced concurrently with irradiation of samples during neutron activation analysis. USAEC Graphite Production Reactor at Douglas United Nuclear, Inc., Hanford, Wash. - and Washington State University TRIGA III Research Reactor

cially when the chemical form of the element being traced is unknown. It is the intention of this work to infer the chemical state of gold in the real system from the behavior of the tracer in controlled experiments.

The scheme for the preparation of sea water solutions equilibrated with ^{195}Au in gold carrier is shown in Fig. 2-1. Gulf of Alaska sea water (Cl $^{o}/_{oo}$ = 18) was used to make up a series of solutions. Water for solutions A and D (Fig. 2-1) was passed through a 0.01 μ HA Millipore filter and oxidized with persulfuric acid similar to the method described by Slowey (1966). Sea water was refluxed for 5 min after the addition of 10 ml 0.1N $K_2S_2O_8$ and 10 ml 0.4N HCl per liter. The solution with all of the gold in the III oxidation state was passed through a column of BIO-RAD AG-1-X8, 100-200 mesh ~~strong anion exchange~~ resin to obtain gold-free sea water.

Soluble gold, a mixture of ^{195}Au and native gold, was added to solution D to a volume of one liter. The initial concentration was 100 μg Au/l with an activity of 106440 c/min/μg Au. Water for solution B was passed through a 0.45 μ HA Millipore filter. Solution C was unfiltered (Fig. 2-1).

A mixture of ^{195}Au and native gold in solution as $AuCl_4^-$ was added to solutions B and C. The final concentration was 83.3 μg Au/l with an activity of 182, 250 c/min/μg Au. The gold originally present was insignificant compared to the amount added. The pH of all solutions was adjusted to 8.0 ± 0.2.

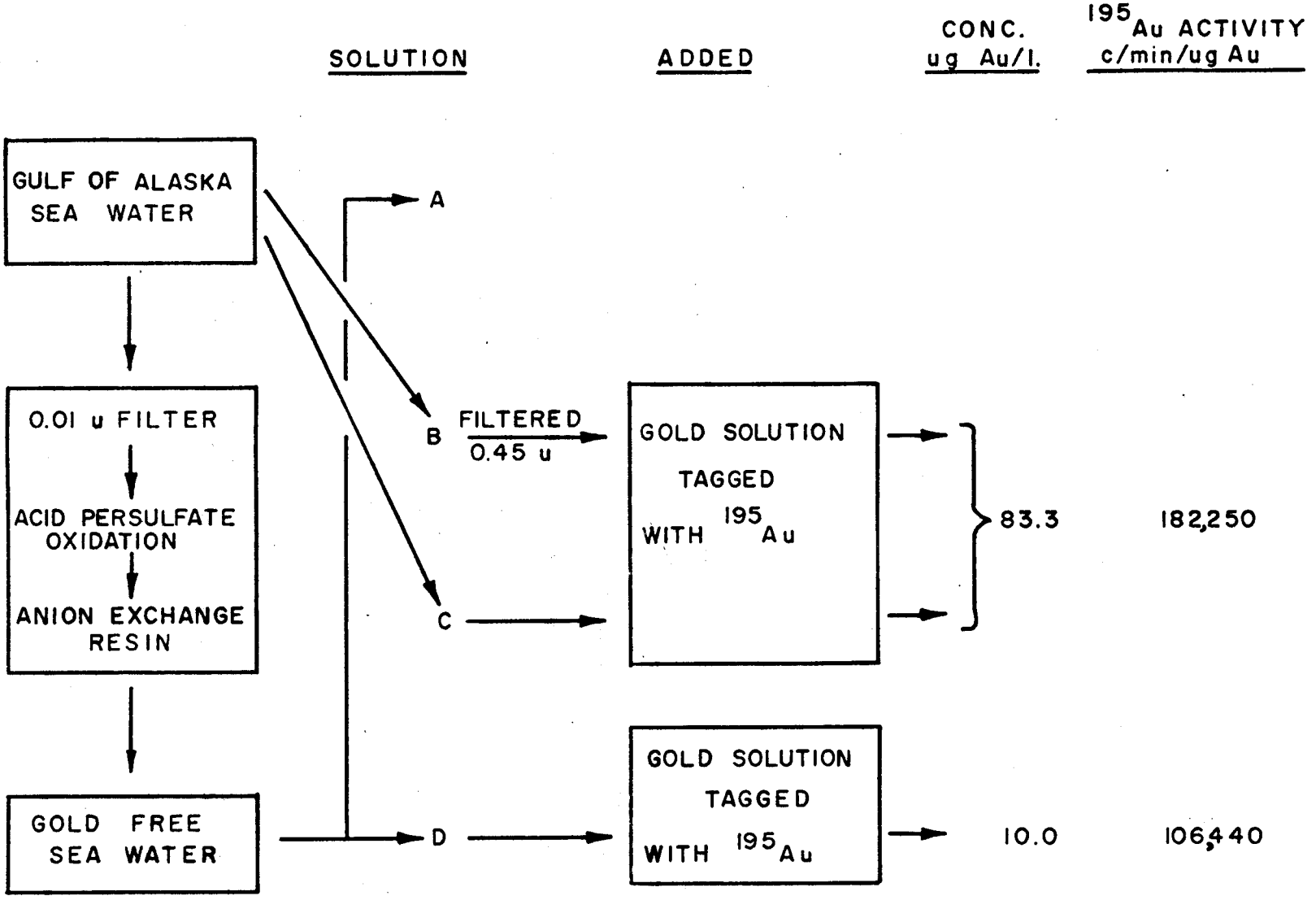

Fig. 2-1 Scheme for preparation of solutions used to characterize gold in sea water.

INSTRUMENTATION AND METHODS

A Nuclear-Chicago, Model 8775, Scaler/Timer coupled to a Harshaw, 7.6 cm x 7.6 cm NaI(Tl), scintillation well detector, Type 12 SW12-W4, shielded by 10.2 cm of lead was used to measure the activity produced by the radioactive tracers. Background activity of ca 350 c/min was common with an applied voltage to the detector of 1950. The background activity was determined at least once before and after each set of experiments with 100 min counts. The range in background activities over the course of an experiment never exceeded 1%.

Experiments were designed so that total counts of at least 10,000 above background were obtained in a reasonable amount of time (2-20 min). The error associated with 10,000 counts, 1%, is usually small compared to other errors and is not significantly reduced by larger counts. All activities were corrected for background and for radioactive decay.

REMOVAL OF SUSPENDED PARTICULATE MATTER

Centrifugation and filtration both remove particulate matter from suspension. However, because the processes depend on different principles (size vs. density), they are not always directly comparable. Filtration was commonly used for samples of more than a few hundred milliliters. A filter pore size of 0.45 μ was chosen as a working definition of particulate. A major consideration with small samples is contamination. This can be greatly reduced by centrifugation because the separation process can often be done in the storage container.

Several solutions were treated both by filtration and by centrifu-

gation in order to compare the two methods. Five milliliters of solution C were centrifuged for 20 min at 2500 rpm (International Clinical Centrifuge Model CL) followed by removal of 3 ml for counting. Another 5 ml of solution B were filtered through a 0.45 μ filter and 3 ml counted. The experiment was repeated twice and the results were:

	Centrifuged		Filtered
	148 c/min/ml		116 c/min/ml
	146		127
	152		120
Average	149 ± 4 (σ)	Average	121 ± 6 (σ)

The initial activity was 865 ± 25 (σ) c/min/ml. The two processes produce reproducible results but differ by 19%.

Stokes' Law for settling rates was used to calculate an effective particle size for the centrifugation method. Assuming a density range of 1.05 to 1.25 for the particulate matter, a figure of 0.2 ± μ was calculated compared to the 0.45 μ filter used. It would appear from the experiment that either the centrifugation was not as efficient as calculated or that the filters were removing more than just particulate matter from the solution. The latter case was examined.

One hundred milliliters of solution C were filtered through a stack of five 0.45 μ HA Millipore filters (mixed esters of cellulose). The filters were rinsed with distilled water and the reservoir removed. The filter edges were rinsed as each filter was removed individually for counting.

A second 100 ml of solution C was adjusted to pH = 1.5 with HCl and

passed through a stack of eight filters. These were rinsed with dilute HCl and counted.

The results are shown in Fig. 2-2. Retention of gold on all filters is noted however the retention is considerably less at pH = 8.

The adsorption of gold on several other materials used in sample handling was checked in a qualitative manner: polyvinylchloride (PVC), surgical rubber tubing, Pyrex, polyethylene, Tygon, leucite, and polypropylene. Most surfaces adsorb less gold from acidified solutions than from sea water with a normal pH of 8.0 ± 0.2. The surgical rubber tubing and the filters were exceptions.

HETEROGENIETY OF GOLD IN PARTICULATE MATTER

The amount of particulate matter in open ocean samples is usually very small. Up to 10 liters may be required to obtain a significant amount. However, in coastal areas and especially glacial fjords, particulate matter may be abundant enough to clog a filter with less than one liter of water. Replicate determinations of particulate weights from the same type of water often show poor reproducibility.

The reproducibility of gold concentrations in solution C was investigated. The solution was sampled for counting after standing three days undisturbed. Then a portion of the water was centrifuged for 20 min at 2500 rpm and sampled. Finally, the original solution was shaken and sampled. Triplicate 1 ml samples were counted for the three cases described.

The results are shown in Table 2-2. The errors are indicative of what can be expected from sampling the real system, even though the

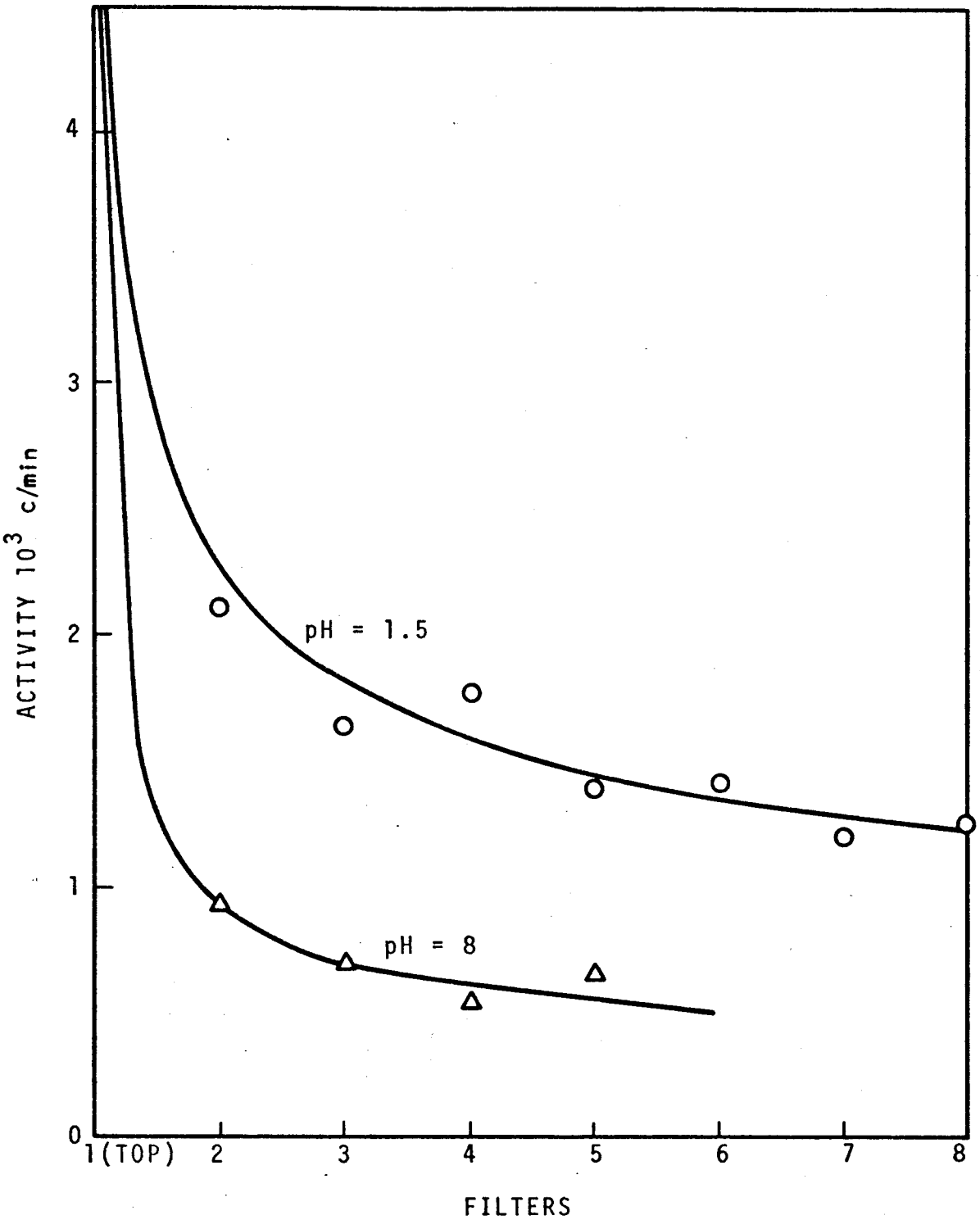

Fig. 2-2 Adsorption of gold by filters from sea water solutions at pH = 1.5 and 8.

Table 2-2

Character of Gold Equilibrated with Sea Water Sample C, Unfiltered, $Cl^{\circ}/_{\circ\circ}$ = 18
^{195}Au Activity, c/min/ml

	Centrifuged	Undisturbed	Shaken
	421	934	9552
	428	881	12415
	426	942	7850
Av. (σ)	425 (3.6)	919 (33)	9939 (2307)
% σ	0.8	3.6	23

concentration of gold in the experiment was somewhat higher than normally found in the oceans. Two significant observations can be made from the experiment. First, it is quite evident the the major portion of the gold in a parcel of water may be associated with particulate matter. Secondly, erratic reproducibility can be expected for gold associated with particulate matter.

IONIC GOLD IN SEA WATER

The ion exchange properties of the strong anion resin, Dowex 1, for $AuCl_4^-$ have been demonstrated by Kraus and Nelson (1954), and used by numerous investigators for the separation and concentration of gold from various solutions including sea water. Burstall *et al.* (1953) used a purified form of Dowex 1, Amberlite IRA-400 to retain $Au(CN)_2^-$. However, the retention of $AuCl_2^-$ is not well documented.

The retention characteristics of gold complexes for the column shape and flow rate to be used in this study were investigated.

Glass columns 7 mm I.D. x 14 cm were segmented into 2 cm sections except for 3 cm top and bottom sections. A 1 cm wad of glass wool was placed in the tapered bottom section. The sections were wrapped in a sheet of Parafilm and heated gently near a flame to obtain a seal. Each column was filled with resin, as needed, to a level 1 cm into the top section. A small wad of glass wool was placed on top of the resin (Fig. 2-3). It was discovered early in the study that rubber is a good absorber of gold even from acidified solutions. Tygon tubing was used instead of rubber and rubber stoppers, where necessary, were covered with Parafilm. Polyethylene reservoirs were used.

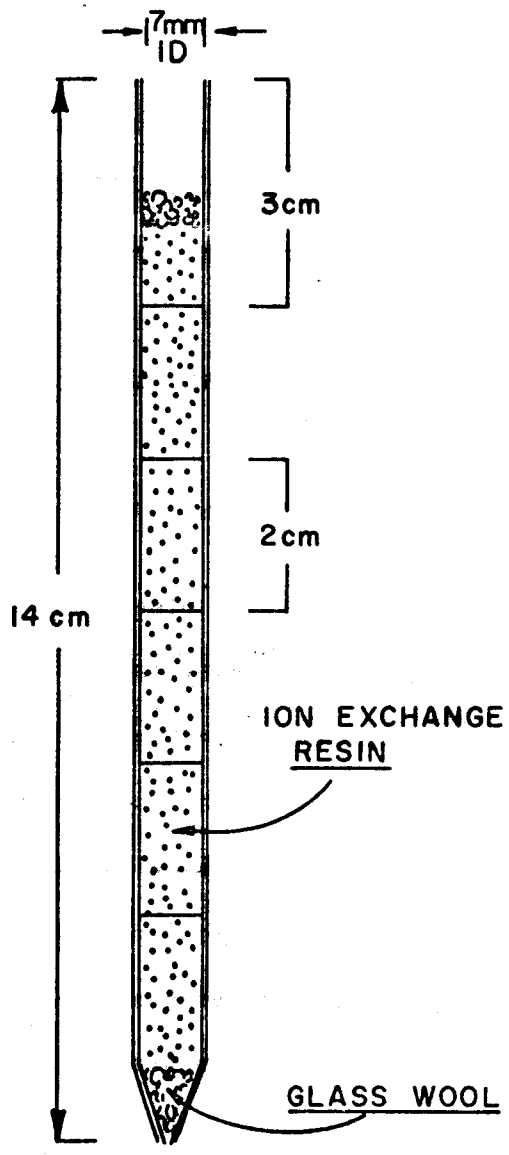

Fig. 2-3 Ion exchange resin column used in laboratory experiments. Columns used in sea water sampling were similar, but not segmented.

RETENTION OF AURIC CHLORIDE ION

Radioactive gold with carrier as $AuCl_4^-$ was mixed with 250 ml of acidified sea water which had been passed through a 0.45 μ filter. The added gold amounted to 1.25 μg Au/l. This mixture was passed through a column of BIO-RAD Ag-1-X8 100-200 mesh strong anion exchange resin at a flow rate of 2 ml/min. The column was rinsed with 10 ml of 2 N HCl and 10 ml of distilled water. The segments of the columns were then separated and counted. The average of three such runs is shown in Fig. 2-4.

RETENTION OF AUROUS CHLORIDE ION

A 32 mg strip of 99.9% pure gold was irradiated for 1 hr in the Washington State University - TRIGA-III-Type research reactor in a flux of 1.5×10^{12} $n/cm^2/sec$, producing the radioactive ^{198}Au. A mixture of $AuCl_2^-$ and $AuCl_4^-$ was produced electrolytically (Fig. 2-5). The cell electrodes had "alligator clamps" soldered to the ends. The gold foil was attached to the anode and a coil of fine platinum wire to the cathode. The cathode assembly was encased in a glass tube open at the bottom. The 125 ml erlenmeyer flask contained 75 ml of 2 N HCl.

The mixture of gold chlorides was produced by 20 ma of current for 60 sec. The resultant solution was ca 15 μg Au/ml. The electrodes were removed immediately following the anodization. Longerich (1967) found nearly a 10:1 ratio of $AuCl_2^-$:$AuCl_4^-$ immediately after anodization under similar conditions. The ratio would be affected by the differences in current to surface area ratio. The current efficiency for the reaction is 100% (Lingane, 1958).

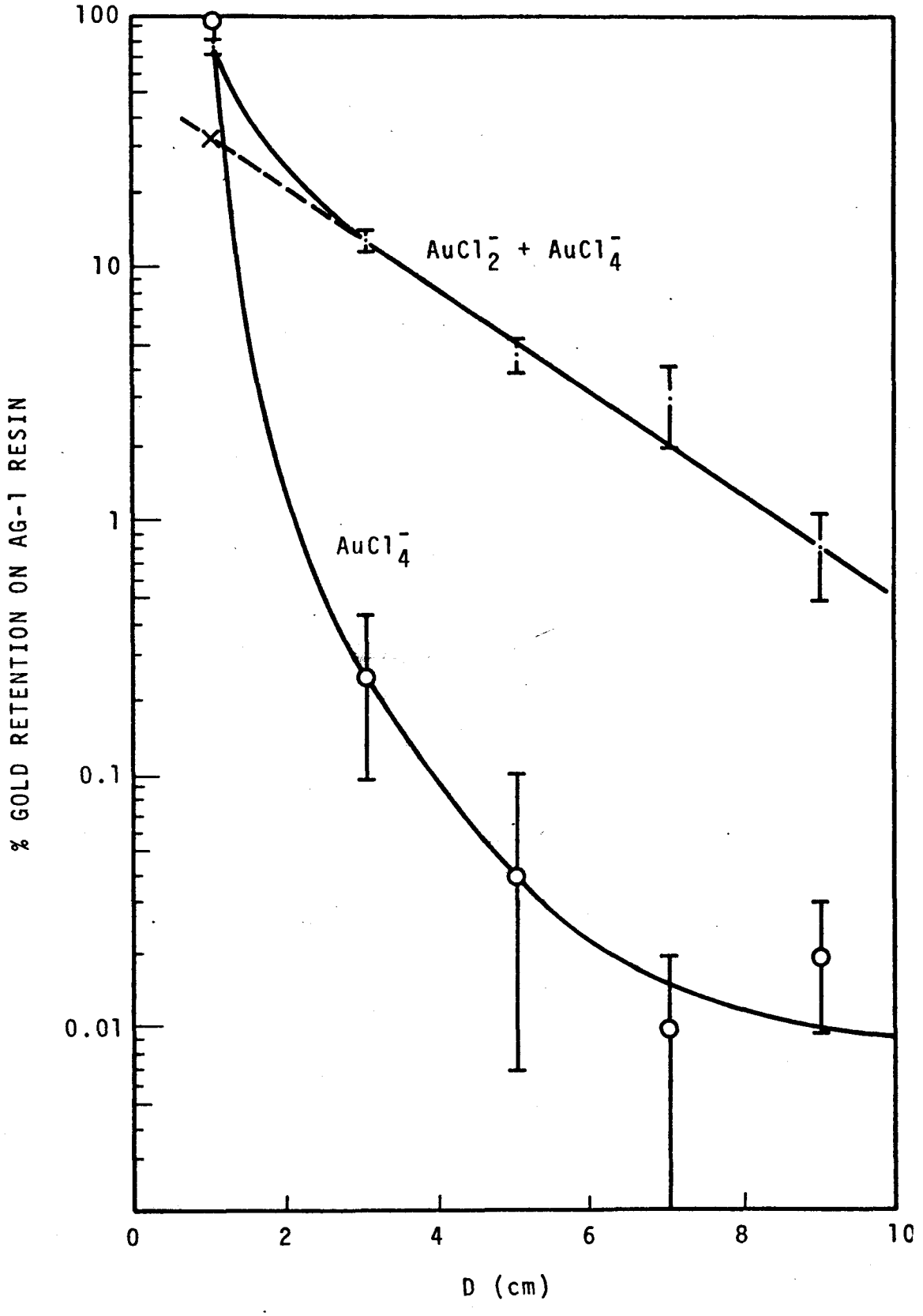

Fig. 2-4 Retention of gold on ion exchange columns. Column distance, D, from the top of the resin.

$I = AuCl_4^-$; $I = AuCl_2^- + AuCl_4^-$

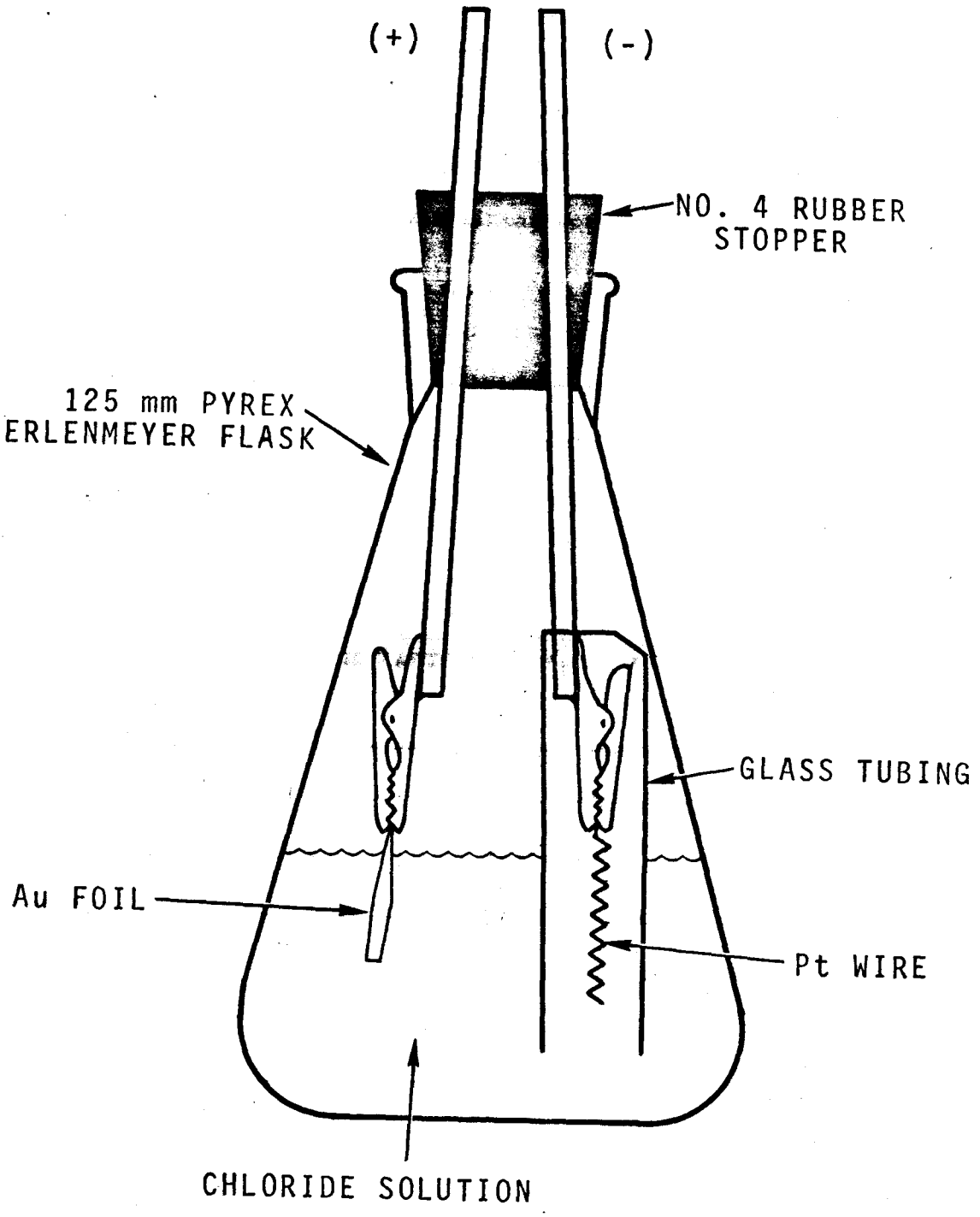

Fig. 2-5 Cell used to anodize gold into solution, a mixture of gold +1 and gold +3.

One milliliter aliquots of the anolyte were diluted with 100 ml of filtered sea water and passed through segmented columns of Ag-1-X8 ion exchange resin. The pH of the solutions was adjusted to ca 1.5. The average of three runs is compared with the retention of $AuCl_4^-$ in Fig. 2-4. By back extrapolation of the linear portion of the $AuCl_2^-$ + $AuCl_4^-$ curve and comparison with the $AuCl_4^-$ curve, it would appear that at least half of the $AuCl_2^-$ + $AuCl_4^-$ mixtures was $AuCl_2^-$. Also, virtually all of the gold was retained on the columns regardless of oxidation state. It appears that the distribution coefficient for $AuCl_2^-$ is not nearly as high as that for $AuCl_4^-$, for which $D = 10^6$ (Kraus and Nelson, 1954).

AUROUS CHLORIDE ANODIZED AT pH = 8

Radioactive gold foil was anodized into sea water at pH = 8 to approximate the state of gold in sea water. The conditions were similar to those previously described, except that the ^{198}Au tracer was produced in a 16 mg strip of gold foil in a graphite production reactor operated by Douglas-United Nuclear at the U.S. Atomic Energy Commission Hanford Site, Richland, Washington.

Anodizing the gold at the pH of normal sea water eliminates the problems of localized high pH during adjustment of an acidified solution with strong base. The locally formed metal hydroxides scavenge gold and may even reduce it to Au°.

Five milliliters of the solution were diluted to 50 ml with sea water and passed through a segmented AG-1-X8 resin column at pH = 8.

The results are shown compared to an experiment where a gold electrode was anodized in acidified sea water in Fig. 2-6.

It was noted that a significant portion of the gold passed through the column. After a time lapse of about two hours the effluent solutions were passed through fresh anion exchange resin columns. The results are shown as continuations of the curves in Fig. 2-6. The initial high retention of the second column (pH = 8) was probably due to an equilibrium adjustment during the time lapse.

The ^{198}Au activity in the effluent was still significant. The solution (pH = 8) was passed through a cation exchange resin AG-50-X8, 100-200 mesh which removed 25% of the activity. The effluent was acidified and put through a fresh AG-50 column removing another 16% of the activity. It is felt that much of the original solution was of a colloidal nature, at least non-ionic.

RETENTION OF GOLD FROM GOLD EQUILIBRATED SEA WATER

Portions of solution D were diluted with filtered sea water and passed through segmented columns of AG-1 and AG-50 at pH = 8 and pH = 1. The results are shown in Fig. 2-7. The retention of gold on cation exchange resin may be a result of the reduction of anionic gold.

$$AuCl_2^- + e^- \rightleftharpoons Au^\circ + 2\ Cl^- \qquad (2\text{-}1)$$

The effect of pH was negligible here.

It is interesting to note the large difference in the amount of gold not retained on AG-1 resin columns, 6.8% for pH = 1 and 15% for pH = 8. A possible explanation is that at pH = 8 there exists an

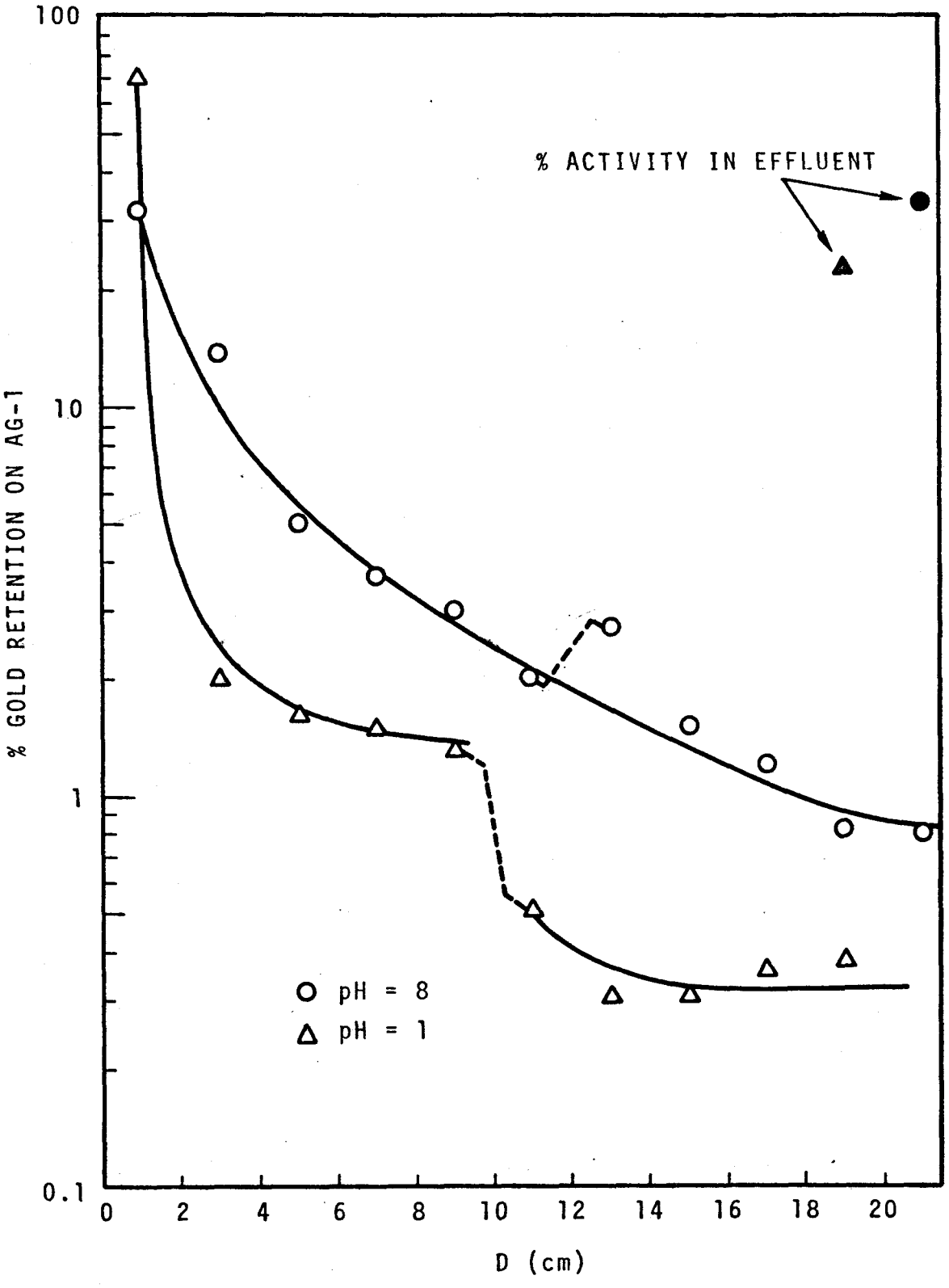

Fig. 2-6 Sea water containing mixtures of gold +1 and gold +3 chlorohydroxy complexes passed through a segmented ion exchange columns at pH = 1 and 8. Dashed line represents solutions put through new columns after 2 hour delay.

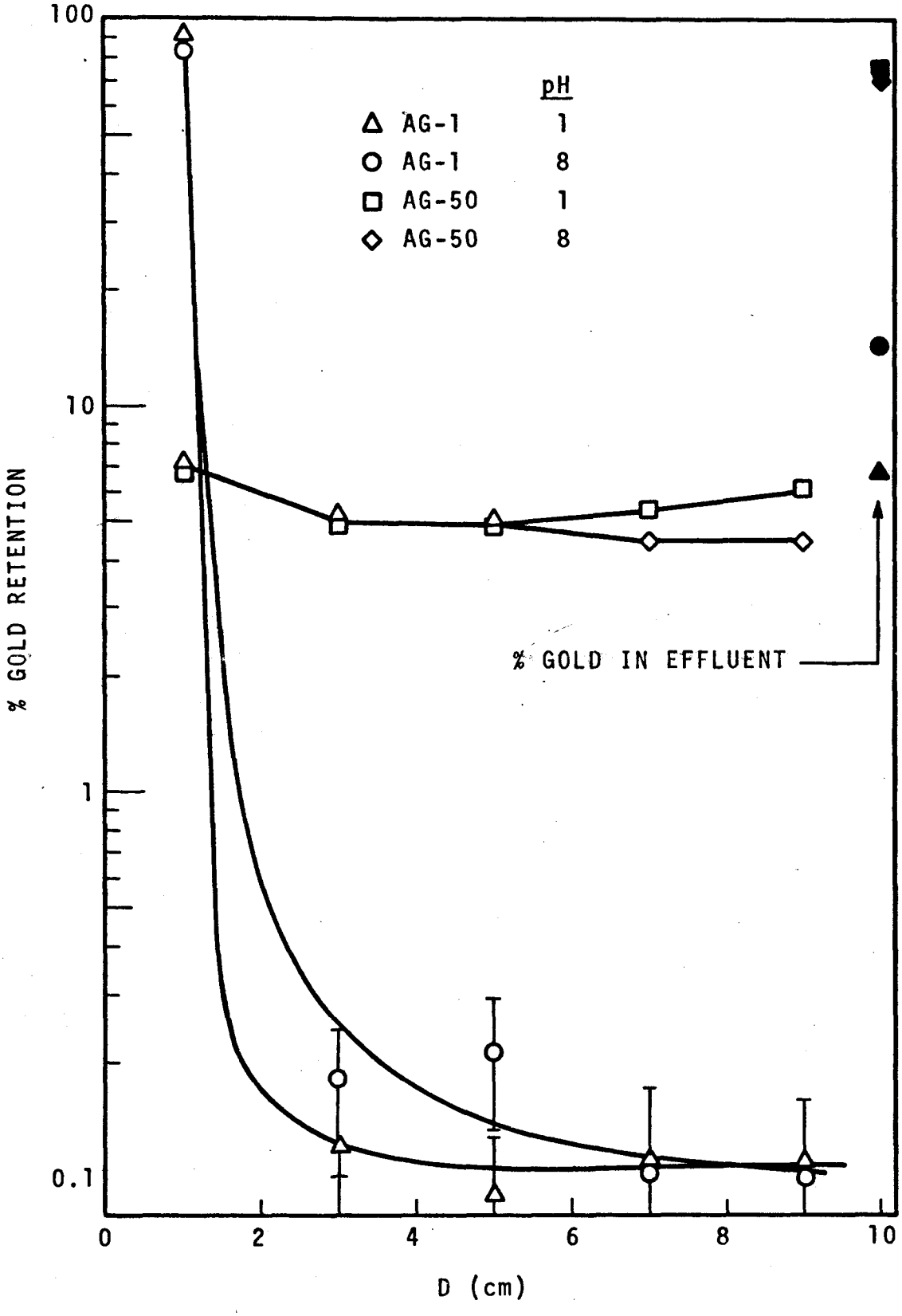

Fig. 2-7 A comparison of the gold retained on anion and on cation resins at pH = 1 and 8. Solid symbols represent the percent of gold which remained in the effluent.

appreciable amount of AuOH with zero charge. Upon acidification, aurous chloride is produced, which can be collected on the strong anion exchange resin.

$$AuOH + H^+ + 2Cl^- \quad AuCl_2^- + H_2O \qquad (2\text{-}2)$$

DIALYSIS OF GOLD FROM SEA WATER

A further attempt to characterize gold in sea water was made by dialysis of 20 ml aliquots of solution D. The solution was placed in a dialysis bag (regenerated cellulose, average pore size, 24A, Van Waters and Rogers Cat. No. 25225-248), which was suspended in a tube containing 20 ml of gold-free sea water (Fig. 2-8). The dialysis bags were prepared by soaking and rinsing in distilled water, then soaking in gold-free sea water.

One milliliter aliquots were taken from the bag and the surrounding water at various times. The average of three such runs is shown in Fig. 2-9. The activity in the outer solution was always less than the activity inside the bag. The average difference at equilibrium was 271 $\pm$ 69 (σ) c/min/ml. The difference in activity between the quantity dialyzed and that which remained in solution was adsorbed on the dialysis bag.

ELECTROPHORESIS OF GOLD FROM SEA WATER

Electrophoresis was cited by Emery and Leddicotte (1961) as a method for separating Au^{+3} from Hg^{+2} and Pt^{+2}, all present as anions in 0.5 N HCl solution. The applied voltage recommended was 3.6 v/cm.

An experiment was set up to look at the possible separation of gold

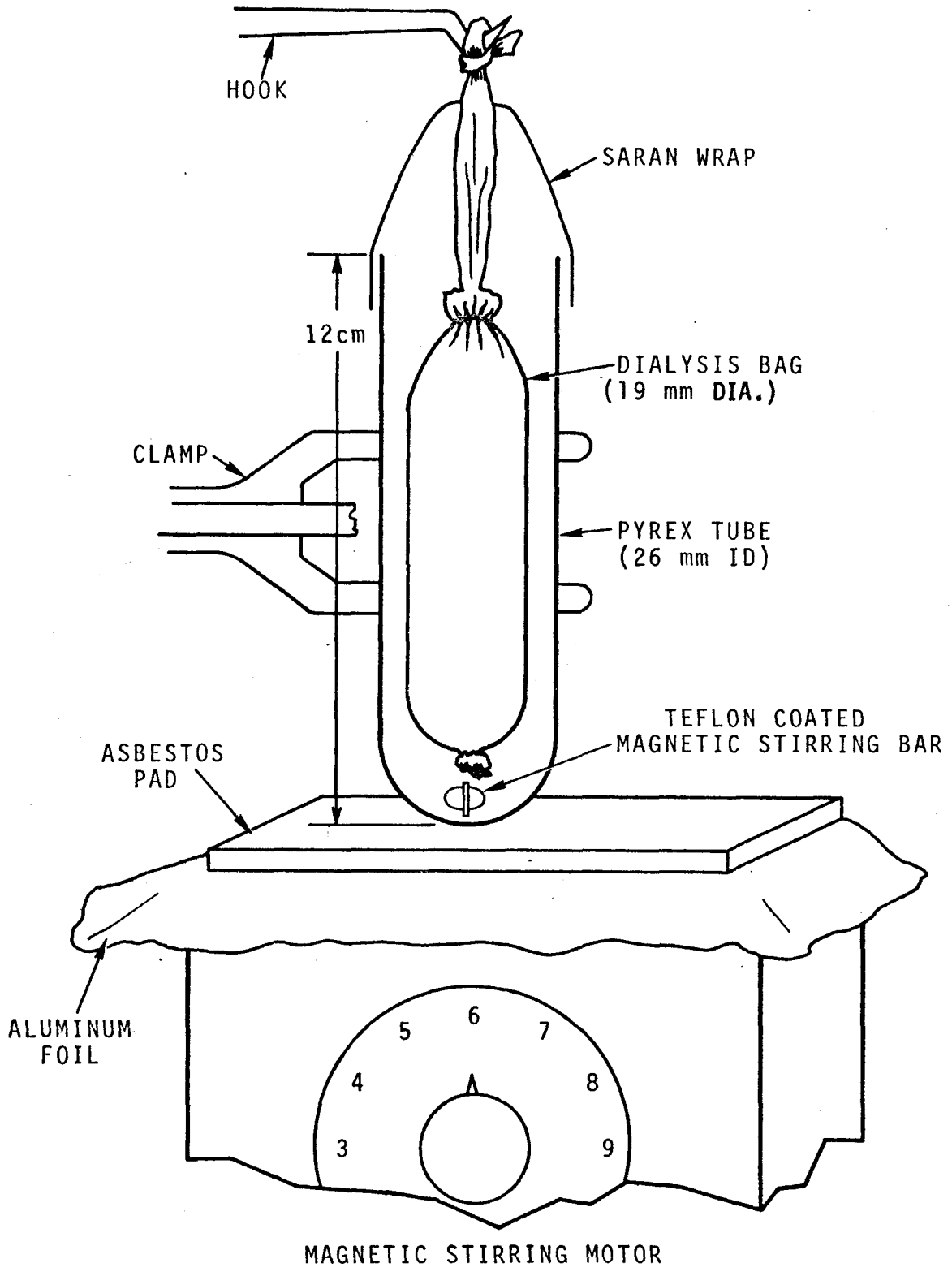

Fig. 2-8 Arrangement for dialysis of gold from sea water contained in the dialysis bag.

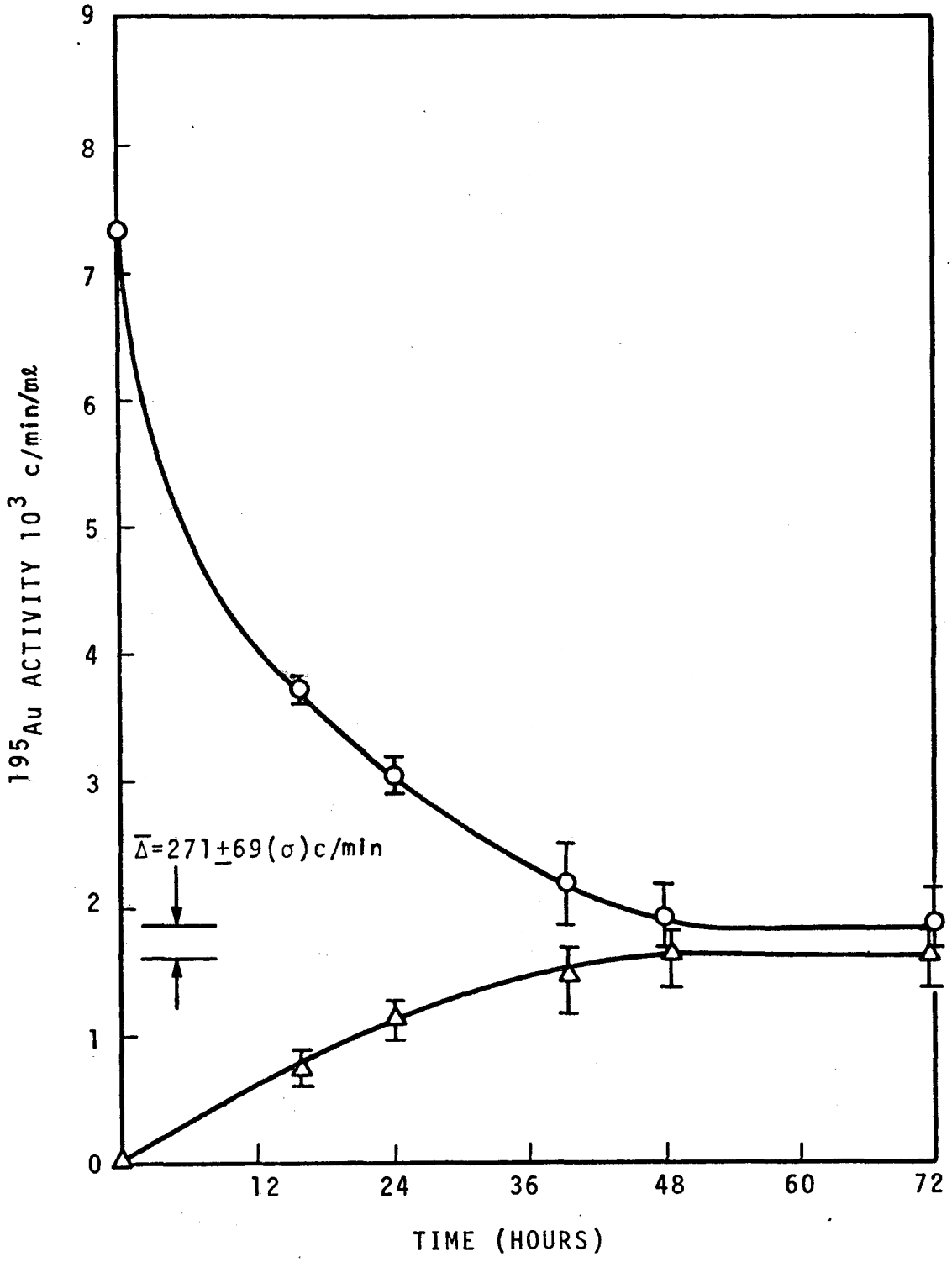

Fig. 2-9 Dialysis of gold from sea water. Difference in amount lost from inner solution, $\bar{\Sigma}$, and outer solution, $\bar{\Delta}$, adsorbed to dialysis bag.

from sea water by electrophoresis. Two strips of chromatographic paper (1 x 16 cm) were crossed in a shallow dish. The ends of one strip were attached to a d.c. power supply, the second strip served as a control. The strips were saturated with gold-free sea water and the excess removed from the dish. Then 10 ml of solution D, pH = 8, were pipetted into the dish covering the middle 4 cm of each strip and approximately 50 volts was applied to one strip for 2 hr. The dish was covered with plastic wrap to reduce evaporation.

At the end of two hours the strips were touched to the side of the dish to allow excess water to run off, then, held with forceps, quickly dried under infra-red lamps. The strips were sprayed with a clear film and cut into 2 cm sections for counting. The average of three such runs is shown in Fig. 2-10.

The differences, Δ, between corresponding sections of the charged strip and the control strip are plotted in Fig. 2-11. A noticeable enrichment at the positive end of the strips was noted; however, the overall activity in the solution was not appreciably depleted. The migration of the ionic gold to the negative end of the strips was noticeably retarded.

If ionic gold in sea water is present mainly as -1 anions, e.g., $AuCl_2OH_2^-$, or $AuClOH^-$, no separation of gold II and gold III would be expected. Indeed, Fig. 10 shows only one minimum. It would appear that little or no cationic gold is present.

LIQUID-LIQUID EXTRACTION OF GOLD FROM SEA WATER WITH ORGANIC SOLVENTS

A possible explanation for the failure of soluble gold to be picked

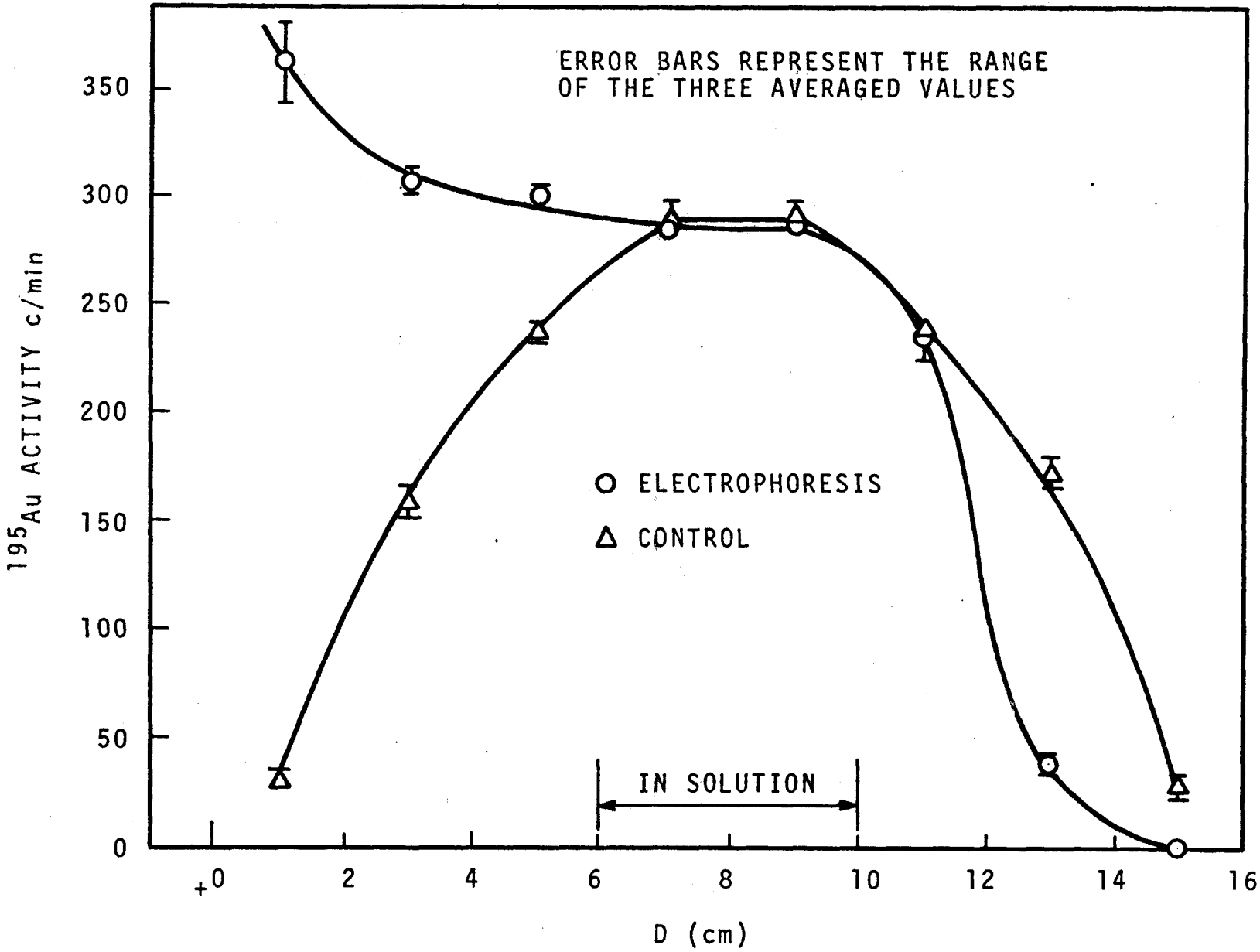

Fig. 2-10 Gold separated from solution by electrophoresis. Distance, D is 2 cm segments arbitrarily measured from positive end of strip under potential.

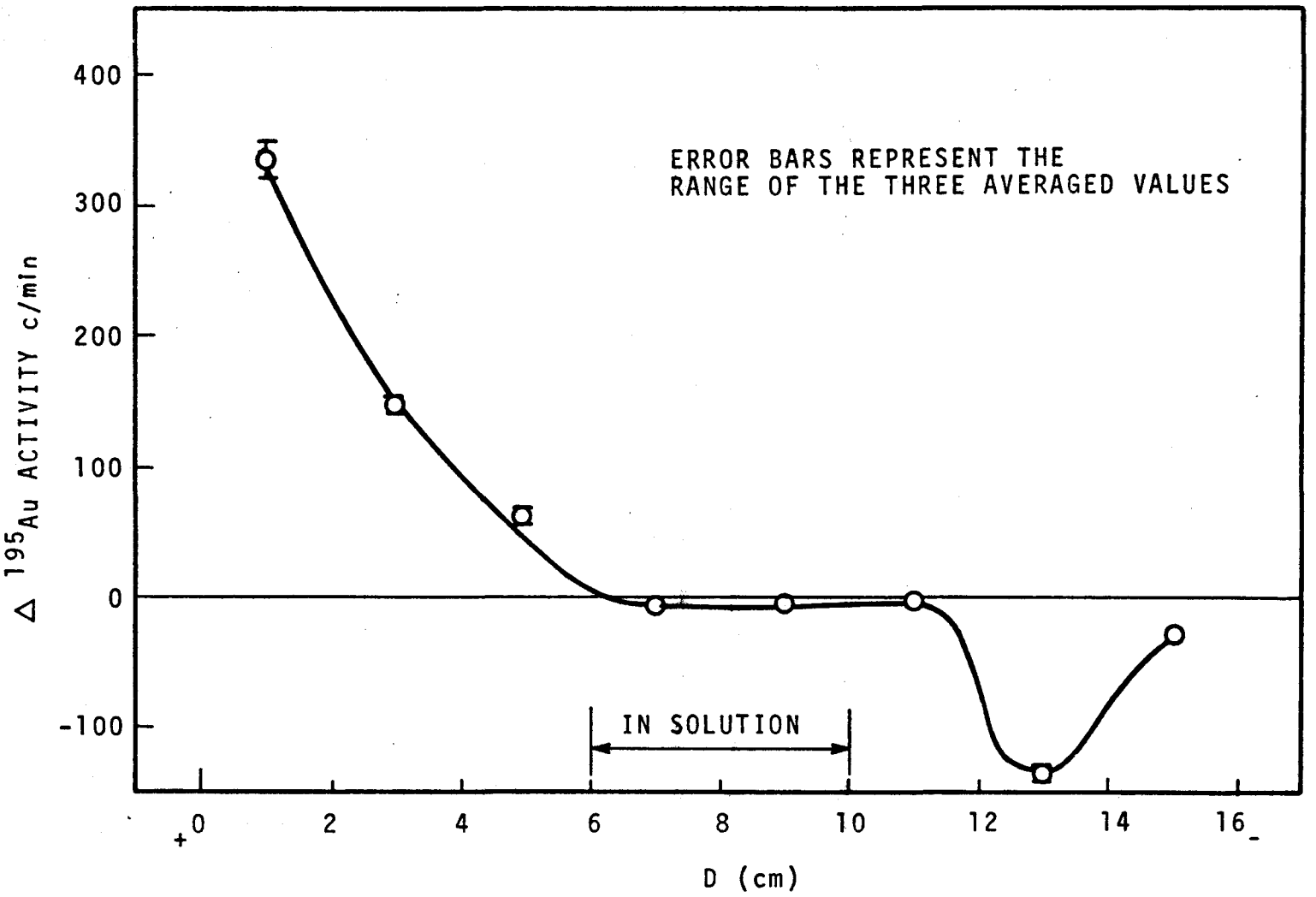

Fig. 2-11 Difference between strip under potential and control strip for gold removed from solution by electrophoresis.

up by ion exchange resins is that it is complexed by dissolved organics. Several solvents have been used to extract organics from sea water (Jeffrey, 1968). A relatively non-polar solvent, chloroform, was used, followed by a polar solvent, ethyl acetate. Ethyl acetate is also a very good solvent for gold chlorides in acid solution (Goldberg and Brown, 1950).

Gold-equilibrated sea water (Solution C) was centrifuged (427 c/min/ml) and passed through a column of AG-1 anion exchange resin at pH = 8 to remove particulate matter and ionic gold, respectively. Ten milliliters of the effluent, with an activity of 186 c/min/ml, were shaken in a glass tube with 3 ml of chloroform. One milliliter of the solvent was removed for counting. Only 0.8% of the activity was removed by chloroform. Five milliliters of ethyl acetate were added and 6.5% of the activity was removed.

A second ten milliliters of AG-1 effluent were acidified and treated similarly with 1.1% of the activity removed in chloroform and 52% in ethyl acetate.

A ten milliliter portion of the sea water solution, which was acidified prior to being passed through a column of AG-1 anion exchange resin, was treated as before. The chloroform removed 1.7% of the activity and the ethyl acetate, 29%, which is only 1.5% of the original solution. It would appear that if gold is organically complexed that the organic matter is not extractable in the solvents used.

The significant increase in gold extracted in ethyl acetate following acidification is probably a result of gold being released from non-ionic complexes with the shift in pH (equation 2-2).

SORPTION PROBLEMS ASSOCIATED WITH SAMPLING THE NATURAL SYSTEM

The laboratory results must relate to the natural system to be pertinent. Therefore a sampling program was designed to determine the various forms of gold in the marine environment in order to elucidate its geochemistry. Several tracer experiments pertaining to the sampling will be covered here.

Sampling Bottles

Five liter Van Dorn-type water sampling bottles (CM^2, Inc. Cat. No. 806) were used. Polyvinylchloride (PVC) and rubber are the principle materials which come in contact with the water. Both materials will absorb gold over a period of time, however the surface to volume ratio is relatively small and little loss of gold would result if the sampling device is pre-equilibrated with sea water and contact time minimized.

Sample Storage

Sample storage was the second consideration. Glass, polyethylene and polypropylene were examined. The plastics are preferred aboard ship because of the breakage problems associated with an "unstable platform." Contaminating elements in plastics are nearly unleachable into most solutions which would ordinarily be stored in them.

Contaminants can be leached from glass even after aging. This is most prevalent on ground joints and glass frits.

A loss of nearly 75 percent of the gold in a solution stored in polyethylene in a period of three weeks was reported by Hummel (1957). Schutz and Turekian (1965) found little loss of selenium, silver, cobalt, cesium, zinc, chromium, or antimony stored in Pyrex bottles. These

results were confirmed by Robertson (1968a) for cobalt, cesium, silver, zinc and antimony. However, significant sorption was found for uranium, iron, scandium, and indium stored in Pyrex glass. Robertson (1968a) found that acidification of sea water in polyethylene bottles greatly reduced loss by sorption of all elements studied except scandium and uranium.

Sorption of gold from sea water stored in Pyrex glass and polyethylene was studied using ^{198}Au as the tracer. Glass-stoppered Pyrex bottles were washed with Calgon and hot aqua regia, then rinsed with copious amounts of triple distilled water. The screw-cap polyethylene bottles were washed with Calgon and rinsed with dil. HCl prior to rinsing with distilled water. Strong acids were avoided in cleaning polyethylene. Hume (1967) reported that conc. HNO_3 conditions polyethylene to behave as an ion exchanger.

Filtered Gulf of Alaska sea water was spiked with the tracer in gold carrier. Two series of solutions were prepared for both types of containers with pH equal to 1.5, 4, and 8. The total concentration of gold in the first series was 1 µg Au/l and 0.1 µg Au/l for the second. One milliliter aliquots were removed from the original 50 ml for counting. The sorption was followed for one week (Fig. 2-12).

Both glass and polyethylene to a greater extent showed sorption of gold at pH 4 and 8. Very little difference between the two types of containers was seen at pH = 1. Loss to sorption at 1 µg Au/l was 14% and at 0.1 µg Au/l less than 5% for the acidified samples. Equilibrium was established quickly for the solutions of pH = 1, but had not yet reached equilibrium for pH = 4 and 8 at the termination of the experiment.

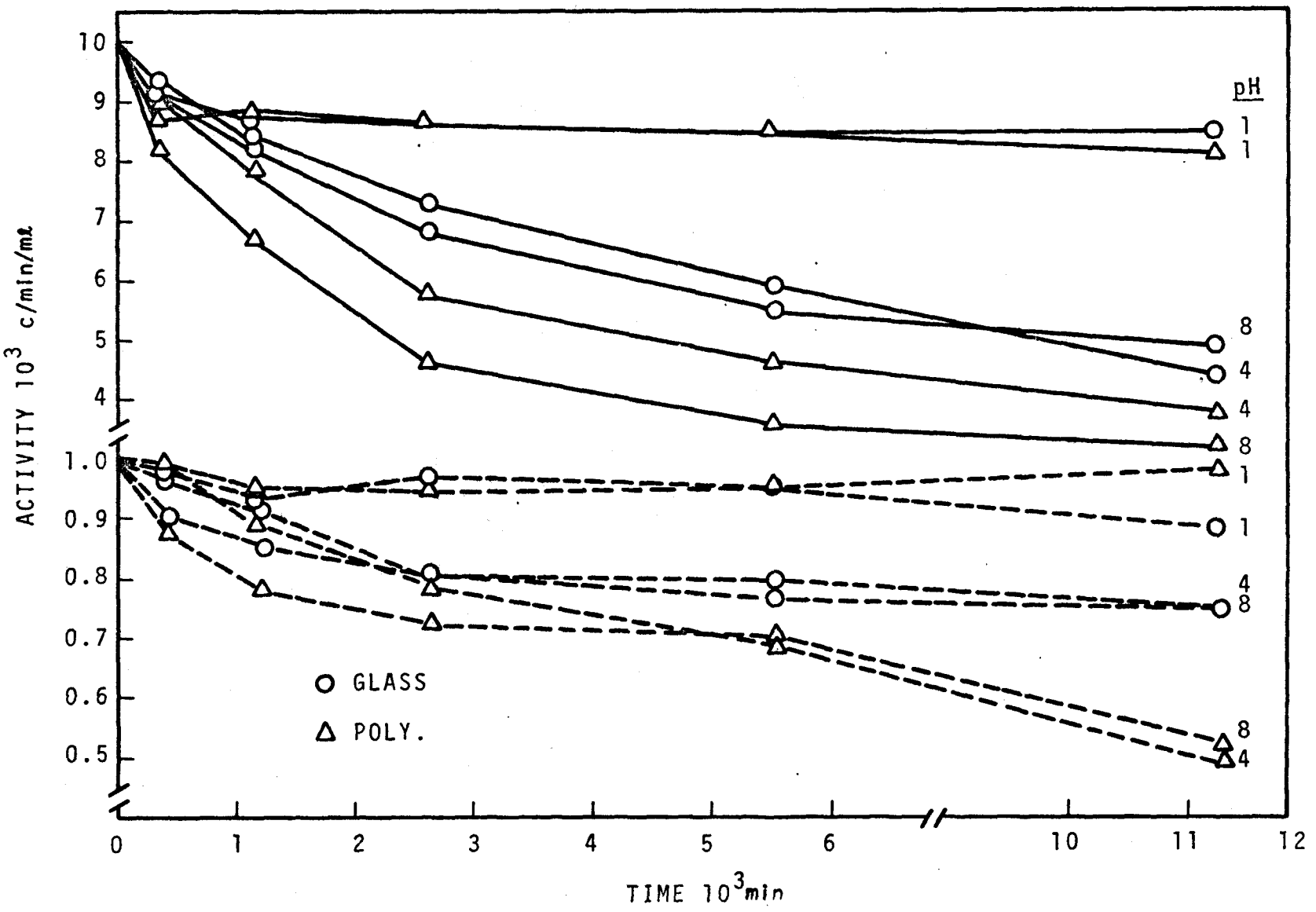

Fig. 2-12 Adsorption of gold on the walls of Pyrex and polyethylene containers at pH = 1, 4, and 8.

It was found that most of the gold lost to sorption from solutions stored at pH = 8 could be returned to solution after being acidified to pH = 1.5 for 24 hours.

Solution D was stored in polypropylene centrifuge tubes at pH = 1.5 and pH = 8. There was no loss of activity at pH = 1.5 at the end of two weeks; however, there was a decrease in the ^{195}Au activity stored at pH = 8 of 8%. Five milliliters of concentrated hydrochloric acid is sufficient to lower the pH of a liter of sea water to about 1.5.

SAMPLE ANALYSIS

Neutron activation analysis, NAA, was chosen for this study because of the sensitivity (sub-parts per trillion), small sample size required, and accuracy. Native gold, element number 79, is 100 percent ^{197}Au, with a 96 barn cross-section for thermal neutrons (Lederer et al., 1967). The interaction of thermal neutrons with ^{197}Au produces ^{198}Au, which decays with a half-life of 2.7 days by beta emission to ^{198}Hg. The amount of gold present in the sample was determined by comparison of the 412 eV photo-peak area of the sample with that of a gold standard. The concentration in the sample can also be calculated from flux data, however corrections must be made for loss of ^{198}Au due to the production of ^{199}Au. The cross-section for ^{198}Au is about 26,000 barns. The loss by production of ^{199}Au amounts to several percent (Ricci and Dyer, 1964; Cabell and Wilkins, 1969).

NAA was used by Goldberg and Brown (1950) to determine gold in meteorites. A comparison of NAA with conventional methods for trace elements in marine organisms was given by Fukai and Meinke (1959).

Schutz and Turekian (1965) measured a number of trace elements in sea salts by NAA. The method was also used by Funk et al. (1969) for trace element work in aquatic environments. Robertson et al. (1968b) applied NAA to a number of marine materials for trace elements without chemical separation.

NAA has been used successfully for gold in geological materials by a number of investigators and is especially well suited for samples with low gold content.

A non-destructive NAA method was used by de Lange et al. (1968) to determine gold in ore. Sheberbakov and Perezhogin (1963; 1964) used NAA to analyze a large variety of geological materials. Gold concentrations in marine sediments have been reported by Crocket et al. (1968), and Harriss et al. (1968). Values range from ca 0.2 to 8.3 ppb in manganese nodules and 1.8 to 3.1 ppb in marine sediments.

SAMPLING PROCEDURES

Equipment

Water samples were collected in polyvinylchloride Van Dorn-type water sampling bottles (General Oceans, CM^2, Inc. Cat. No. 806). The bottles were thoroughly cleaned with Calgon, rinsed with distilled water, 10% HCl, and distilled water again. The bottles were allowed to equilibrate with sea water for about 12 hours prior to sampling. All metallic parts on the bottles were coated with a Krylon clear spray prior to use.

All polyethylene containers and Tygon tubing used in the storage and transfer of water were rinsed with dilute HCl and distilled water. All glass apparatus was boiled in aqua regia ($HCl:HNO_3$ = 3:1) and rinsed

with distilled water. All metal parts, clamps, spatulas, forceps, etc. were dipped in a clear vinyl to prevent contamination. Filters were soaked overnight in dilute HCl and rinsed in distilled water following the procedure outlined by Strickland and Parsons (1965) for filter preparation.

Sediment samples were collected with a Shipek grab and a piston corer. No special treatment was given either piece of apparatus. They were in reasonably good condition. Plastic core liners were used.

SAMPLE HANDLING

A maximum of four sampling bottles were used on a cast. This allowed ample time for the samples to be removed from the bottles within about 15 minutes after initial contact. Most of the samples were stored in polyethylene Cubitainers (Hedwin, Inc.). All samples stored for more than a few hours were adjusted to pH = 1.5 with concentrated hydrochloric acid (5 ml/l). Some samples were stored in glass-stoppered Pyrex bottles for freeze-drying of the salts, and some in polypropylene centrifuge tubes from which the particulate matter was to be removed by centrifugation.

Sea water was filtered through 0.45 μ HA Millipore filters (47 mm dia.) to collect particulate matter for gold analysis. The amount of water filtered varied from one to ten liters, depending upon the amount of particulate matter present. The filters were rinsed with distilled water and placed in Millipore plastic petri dishes. The filters were returned to the laboratory, where they were dried, first in a vacuum oven for two hours at 65°C, 300 torr, and then overnight in a vacuum

desiccator before being weighed.

Ionic gold was determined by acidifying one liter of each filtered sample and putting it through a column of BIO-RAD strong anion exchange resin (AG-1-X8, 100-200 mesh) at a flow rate of about 2 ml/min.

The resin was pre-conditioned with three alternate washes of 10 ml each of 2 N NH_4OH and 2 N HCl ending with the HCl wash. The columns were the same as shown in Fig. 2-3 except that they were not segmented and the glass wool was replaced with polyethylene frits.

The resin columns were rinsed with distilled water, then extruded into polyethylene snap-top capsules. The resin was returned to the laboratory and dried under vacuum and desiccation.

Sea water was returned to the laboratory for analysis of total gold in the samples. Water from ACONA Cruise 074, both filtered and unfiltered, was acidified and stored in 200 ml glass-stoppered Pyrex bottles. The salts were dried by pipetting 100 ml of sea water into a 500 ml round-bottomed flask and freezing in dry ice and acetone, while rotating the flask (Bolter et al., 1964). Four flasks at a time were attached to a cold-finger and evacuated (Fig. 2-13). About 10 hr were required to completely dry the salts, which were then tapped into polyethylene snap-top capsules.

Acidified sea water from ACONA Cruise 089 and U.S. Coast and Geodetic Survey RAINIER Cruise Sp-1-70 was returned to the laboratory and dried under infra-red lamps in polyproplyene tubes, then transferred to polyethylene snap-top capsules. A 2/5 dram capsule holds about 1 g of salt, equivalent to about 30 ml of sea water.

Sediment samples were removed from the interior of a grab to insure

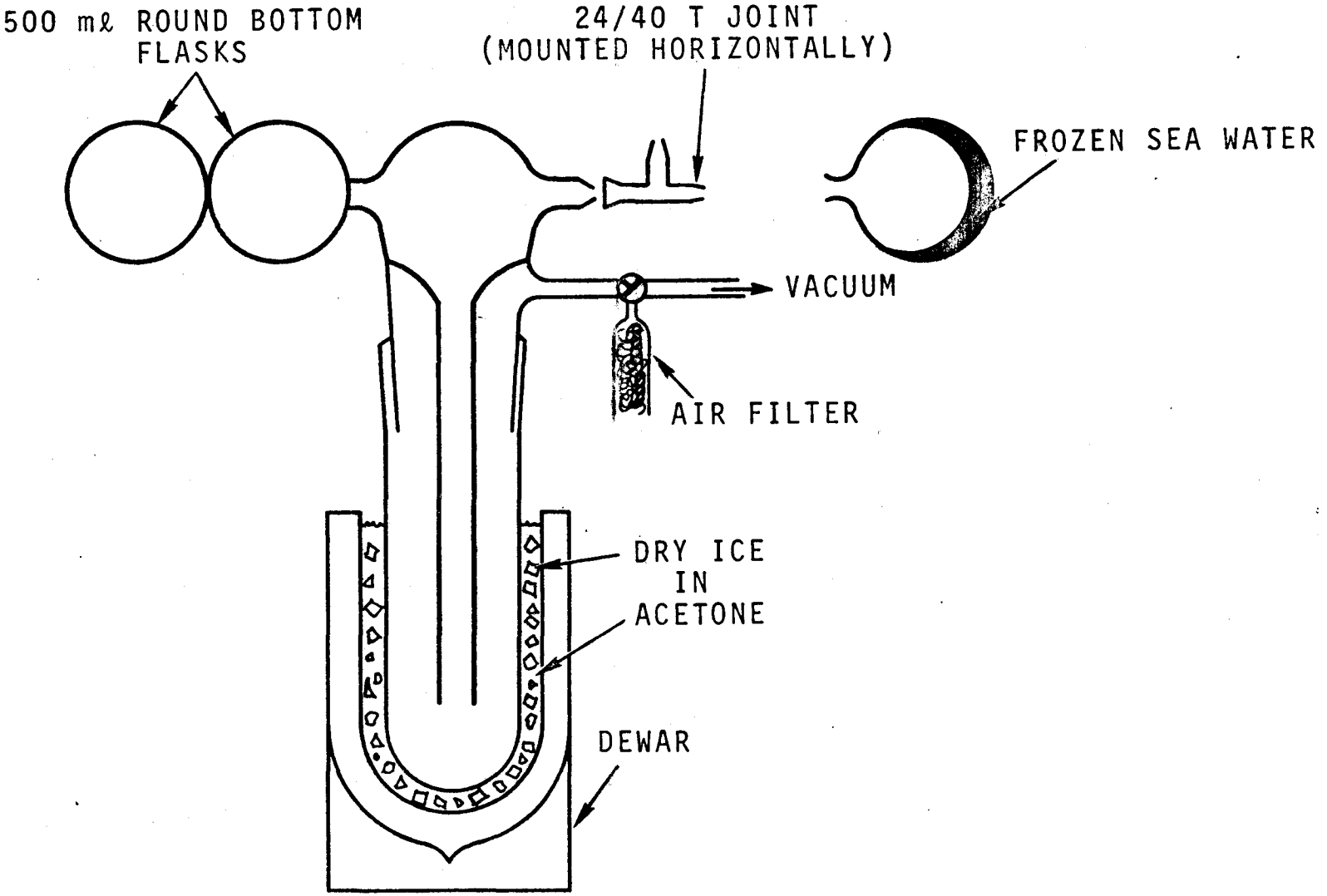

Fig. 2-13 Apparatus used for freeze-drying sea water samples.

that no sediment in the sample had come in contact with the apparatus. The sediment was handled with a nylon spatula and placed in plastic bags.

Cores were extruded from the plastic liners with compressed gas. The cores were split and samples removed from the interior with the aid of a nylon spatula.

The free moisture was removed from the sediments by drying in a Soil Test oven at 120°C for about 24 hr. Some of the samples were sized, using thoroughly cleaned stainless steel sieves, then stored in plastic bags.

PREPARATION OF SAMPLES FOR ANALYSIS

All of the samples (salts, resin, filters) were sealed in polyethylene capsules, as were appropriate standards and blanks. The amount of gold in the samples was determined by neutron activation analysis. Most of the sample preparation was done in an Agnew-Higgins laminar-flow clean hood located in a room used only for sample preparation. Polyethylene gloves were worn while handling samples, all metallic objects were coated with a clear acrylic spray or vinyl paint, and all glassware was cleaned with hot aqua regia.

Contamination is an ever-present factor in trace element analysis. A very good discussion of the problem is given by Theiers (1957), and more specifically related to the marine studies by Schutz (1964) and by Robertson (1968a). The conclusions of these and other authors were taken into consideration in this study to reduce contamination to an acceptable minimum.

Standards were prepared by adding 50 µl of a gold chloride

solution, 10^{-7} g Au/ml, to an appropriate matrix (filter, salt, resin or Scotch Magic Mending tape). Standards and blanks were treated the same as samples.

The individual sample capsules were heat-sealed, then placed in Nalgene polyethylene capsules ca 4.5 cm inside diameter and 7.3 cm overall length for irradiation. The tops were then heat-sealed. Depending upon the type of sample capsules used, two or three tiers of capsules were combined in each large capsule.

IRRADIATION

The samples were irradiated with thermal neutrons in an Atomic Energy Commission graphite production reactor at its Hanford Site, Richland, Washington. The integrated flux received by the samples was about 2×10^{18} n/cm^2. Cooling periods of 2 to 10 days allowed short-lived activities to decay sufficiently for safe handling. The cooling periods and major interferring activities are given in Table 2-3. Sulfur-35 was particularly troublesome in irradiated sea salts. Particular care is required to eliminate ^{35}S from the samples and to prevent its migration in the laboratory. Sulfur-35 has a relatively long half-life, 87 days, and is a weak beta emitter. It is produced mainly by the reaction $^{35}Cl(n,p)^{35}S$, and to a lesser extent by the reaction $^{34}S(n,\gamma)^{35}S$. The cross-sections for these reactions are 0.40 and 0.27 barns, respectively (Wang, 1969).

Table 2-3

Irradiation Data Pertinent to Neutron Analysis for Gold

	Cooling Period	Major Interferring Activities & Half-Lives
Filters	2-5 days	^{24}Na, 15h
Resin	4-6	^{82}Br, 36h
Salts	7-10	^{24}Na, 15h; ^{82}Br, 36h; ^{35}S, 87d.

SEPARATION SCHEMES

For the most part, this study was concerned with the geochemistry and analysis of a single element, gold, with no attempt to separate or to measure quantitatively other elements. The general separation procedure was to dissolve and oxidize the sample in an acid chloride solution, followed by separation and purification of the radioactive gold in a carrier. The separation scheme of Goldberg and Brown (1950) was used initially and modified several times. The scheme consisted of an ethyl acetate extraction of auric chloride from an acid solution, evaporation and precipitation of the gold, from a dilute HCl solution with hydroquinone. Radioactive ^{195}Au was added to the gold carrier to check the separation efficiencies in lieu of weighing, similar to a procedure reported by Green et al. (1969). In order to check the reproducibility of the radiochemical separation monitor, ten one milliliter aliquots of gold carrier were pipetted into glass screw-cap vials and dried in a muffle furnace to reduce the gold to the metallic form. The activity and weight of gold in each vial were determined. The average activity was 10, 942 $\pm$ 467 (σ) c/m, and the average weight of gold was 18.16 $\pm$ 0.66 (σ) mg, 4.3% and 3.6% error, respectively. The difference in error is not significant especially when compared to the possible errors resulting from the handling of the sample during the weighing process.

FILTER SEPARATION

1. The irradiated filters were dissolved in 1-2 ml of conc. H_2SO_4 in a 100 ml beaker. Warming under an infra-red lamp accelerated solution.

2. One milliliter of an acid chloride solution containing about 20 mg of gold carrier and about 0.05 μCi ^{195}Au (a sufficient amount to give ≥ 10,000-99 KeV counts in a 30 min counting time) was added.
3. Ten milliliters of aqua regia were added, the beaker was covered with a watch glass, and the solution was refluxed on a hot plate for 20 min.
4. The solution was diluted with about 20 ml of 1 N HCl by washing down the sides of the beaker with a wash bottle containing the dilute acid.
5. After cooling the solution was poured through a short column of strong anion exchange resin. The resin on a filter was placed on a planchet and double wrapped in plastic wrap for counting.

The separation scheme is shown in Fig. 2-14.

RESIN SEPARATION

1. The irradiated ion exchange resin, ca 0.5g, was emptied into a 250 ml beaker and charred by heating with 10 ml of conc. H_2SO_4. The beaker was covered with a watch glass.
2. When the solution began to spatter, 30% hydrogen peroxide was added drop-wise cautiously, by allowing the hydrogen peroxide to run down the side of the beaker. The oxidation process was continued until the solution cleared.
3. The solution was re-heated and re-oxidized until the solution remained clear. (Procedure for degradation of resin recommended by L. E. Wallerstedt, Mallinckrodt Chemical Works, personal communicaton.)

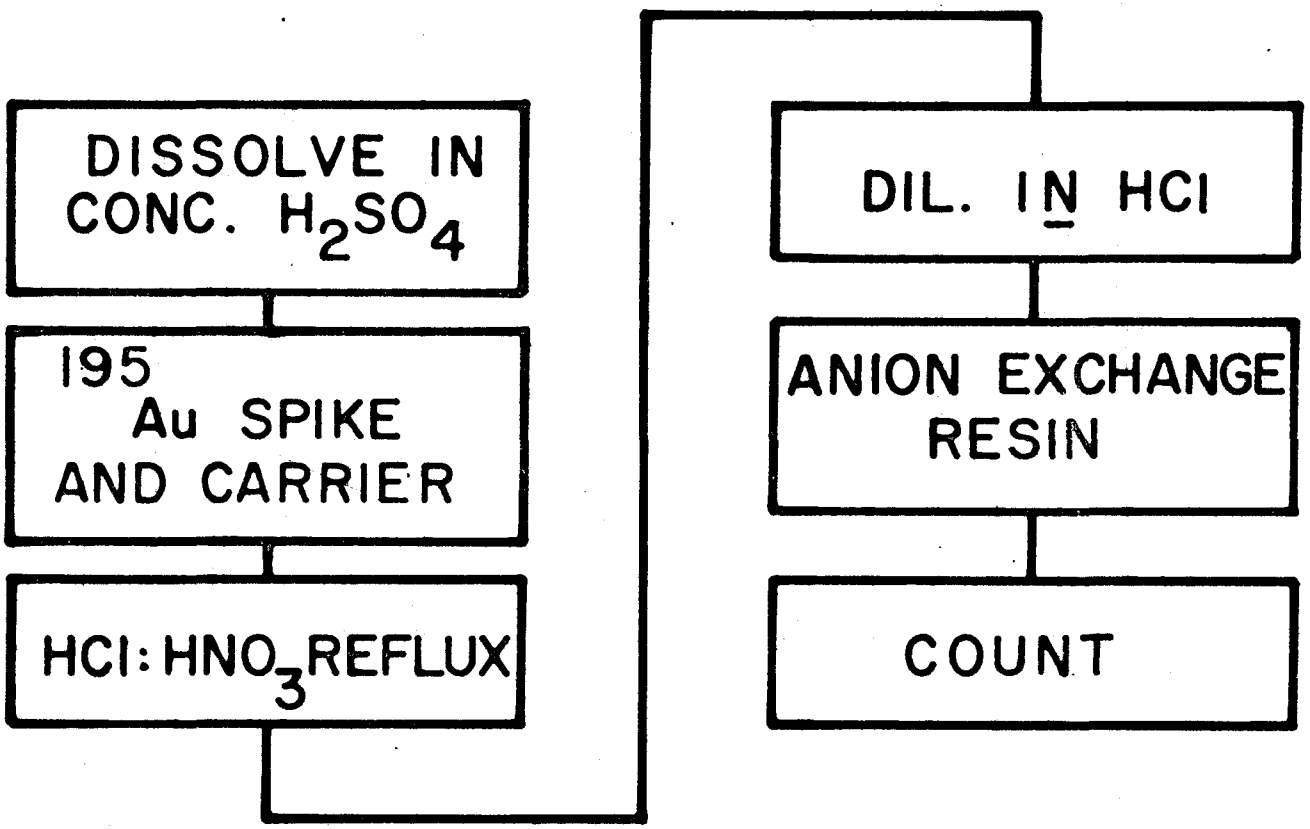

Fig. 2-14 Separation scheme for gold from irradiated filters.

4. One milliliter of carrier and ^{195}Au solution, and 10 ml of aqua regia were added. The beaker was covered with a watch glass and heated to boiling until the white fumes from the sulfuric acid appeared. This purged the halogen acids and nitric acid, ridding the sample of much of the interferring ^{82}Br. At this point, gold began to precipitate from solution as metallic gold. The precipitation process was accelerated by the cautious addition of 30% hydrogen peroxide, which resulted in a mixture of metallic gold and gold oxide. Boiling was continued to coagulate the fine precipitate.
5. The beaker was removed from the heat. After sufficient cooling, the solution was decanted into a liquid waste container. The remaining gold was washed with water and the washings discarded.
6. The gold was redissolved in 10 ml of aqua regia followed by the addition of 10 ml of conc. H_2SO_4 and the covered beaker heated to boiling.
7. The boiling and precipitation process of step 4 was repeated. Very often the coagulation process was slow to occur the second time. The sulfuric acid was diluted cautiously with water after cooling and the gold filtered in a chimney filter apparatus.
8. The gold on a 25 mm filter was transferred to a planchet, and dried under an infra-red lamp. After drying the filter was dissolved with a few drops of acetone and allowed to evaporate.
9. The planchet was sprayed with clear acrylic plastic and double wrapped in Saran wrap for counting.

Separation scheme is shown in Fig. 2-15.

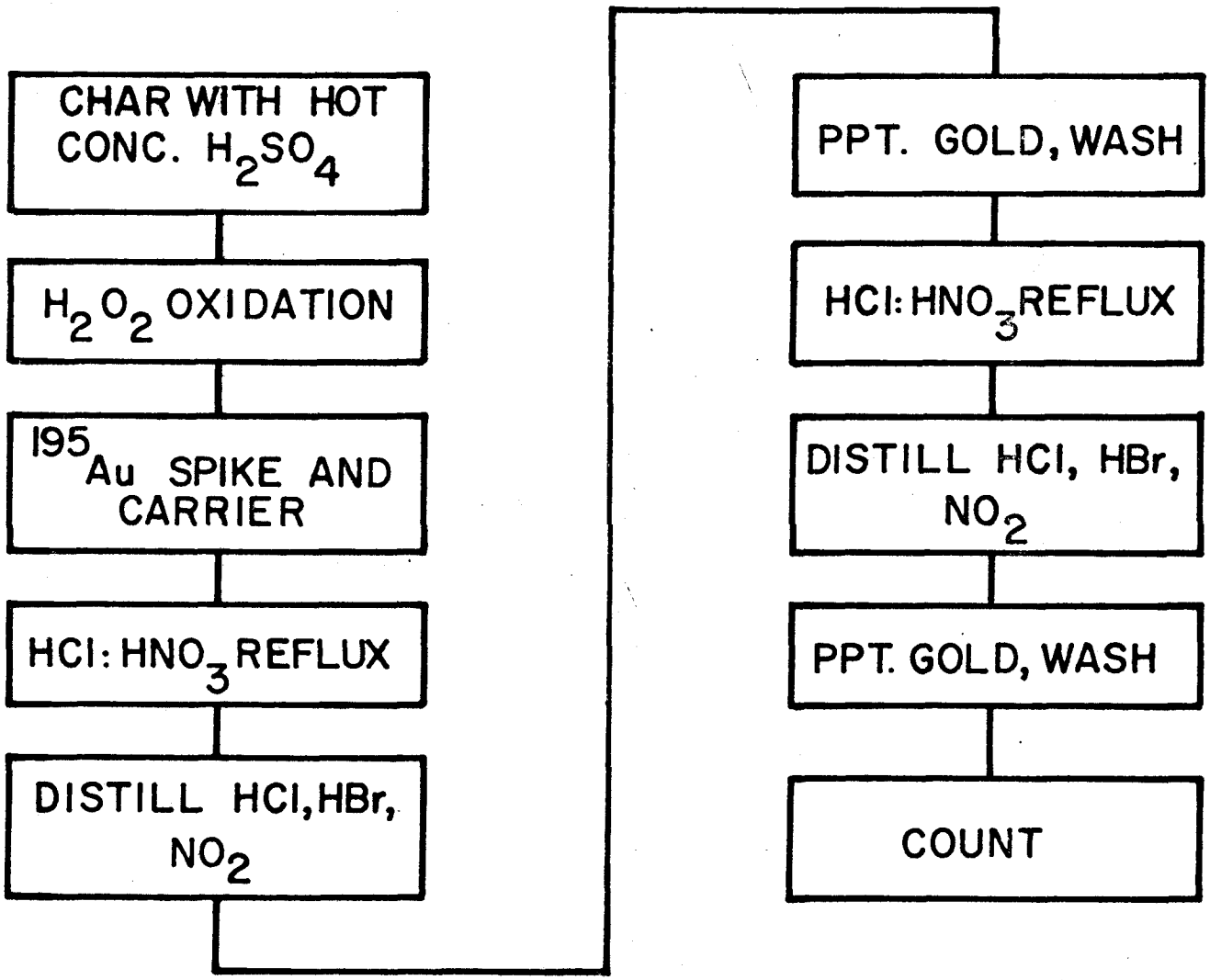

Fig. 2-15 Separation scheme for gold from irradiated ion exchange resin.

SALT SEPARATION

1. The irradiated salt was emptied into a 250 ml beaker and dissolved in a few milliliters of 1 N HCl. Gentle heating accelerated solution.
2. One milliliter of carrier and ^{195}Au solution were added, along with 15 ml of aqua regia. The beaker was covered and the solution refluxed.
3. After the brown fumes from the nitric acid ceased, the solution was allowed to cool somewhat and 10 ml of conc. H_2SO_4 were added.
4. The covered beaker was placed on the hot plate and the halogen acids purged.
5. The precipitation and purification procedure continuing from step 4 of the Resin Separation was then followed.

The separation scheme is shown in Fig. 2-16.

COUNTING PROCEDURES

The photo-peak magnitude of the gold isotopes, ^{195}Au and ^{198}Au, 99 KeV and 412 KeV, respectively, was measured by counting the samples with a Ge(Li) solid state detector-multichannel analyzer system. The samples were counted long enough to obtain at least 10,000 counts in most cases. Blanks and samples of low gold content were counted for a maximum of 40,000 sec on the Ge(Li) diode detector and then an appropriate amount of time using a 7.6 cm x 7.6 cm NaI(Tl) detector. Standards were counted with each group of samples in the same geometry. Most samples could be counted in 4000 to 8000 seconds (ca 1 to 2 hr).

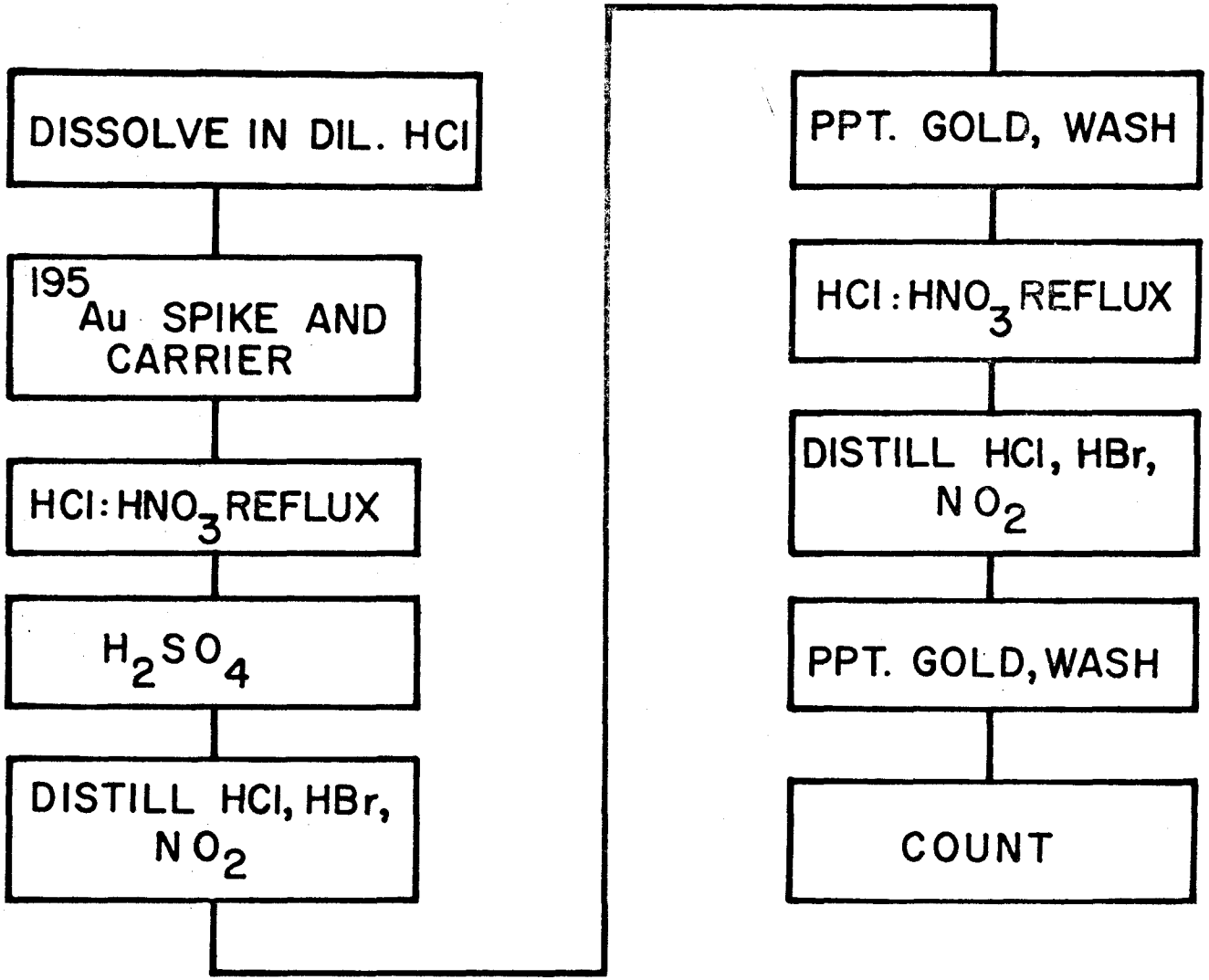

Fig. 2-16 Separation scheme for gold from irradiated sea salts.

INSTRUMENTATION

A 20 cc Nuclear Diodes Ge(Li) diode detector was used in the study in conjunction with a Nuclear Diode Model 101A pre-amplifier and a Tennelec Model TC 202 BLR linear amplifier. The signal was fed into a Nuclear Data ND 2200 4096 channel analyzer equipped with a 100 MHz. analog to digital converter, ADC. The photo-peak of the 1.332 MeV gamma of ^{60}Co was about 3.5% of that obtained using a 7.6 cm x 7.6 cm (NaI(Tl) detector at a distance of 25 cm. The ratio of the peak height to Compton edge was about 16.5:1 and the resolution at full width, half maximum, FWHM, was 2.6 KeV for the 1.332 MeV photo-peak. The detector was mounted vertically and shielded in a cave with 10.2 cm thick walls. The advantages of Ge(Li) solid state spectrometry over NaI(Tl) for resolution have been well documented (Cooper et al., 1968; Robertson, 1968; Funk et al., 1969).

GAMMA-RAY SPECTRUM

A typical sample spectrum is shown in Fig. 2-17. The 99 KeV photo-peak of ^{195}Au was measured as the radiochemical separation monitor. The ^{195}Pt X-rays were produced during the electron capture decay of ^{195}Au.

The amount of gold in the sample was determined by comparison of the 412 KeV ^{198}Au photo-peak area with that of a gold standard. The total peak area method was used to determine nuclide activity.

Other activities encountered, especially with the resin samples, were ^{203}Hg and ^{82}Br. Scandium seems to follow the chemistry of gold to some extent, as the ^{46}Sc photo-peak was seen in many of the samples. Its

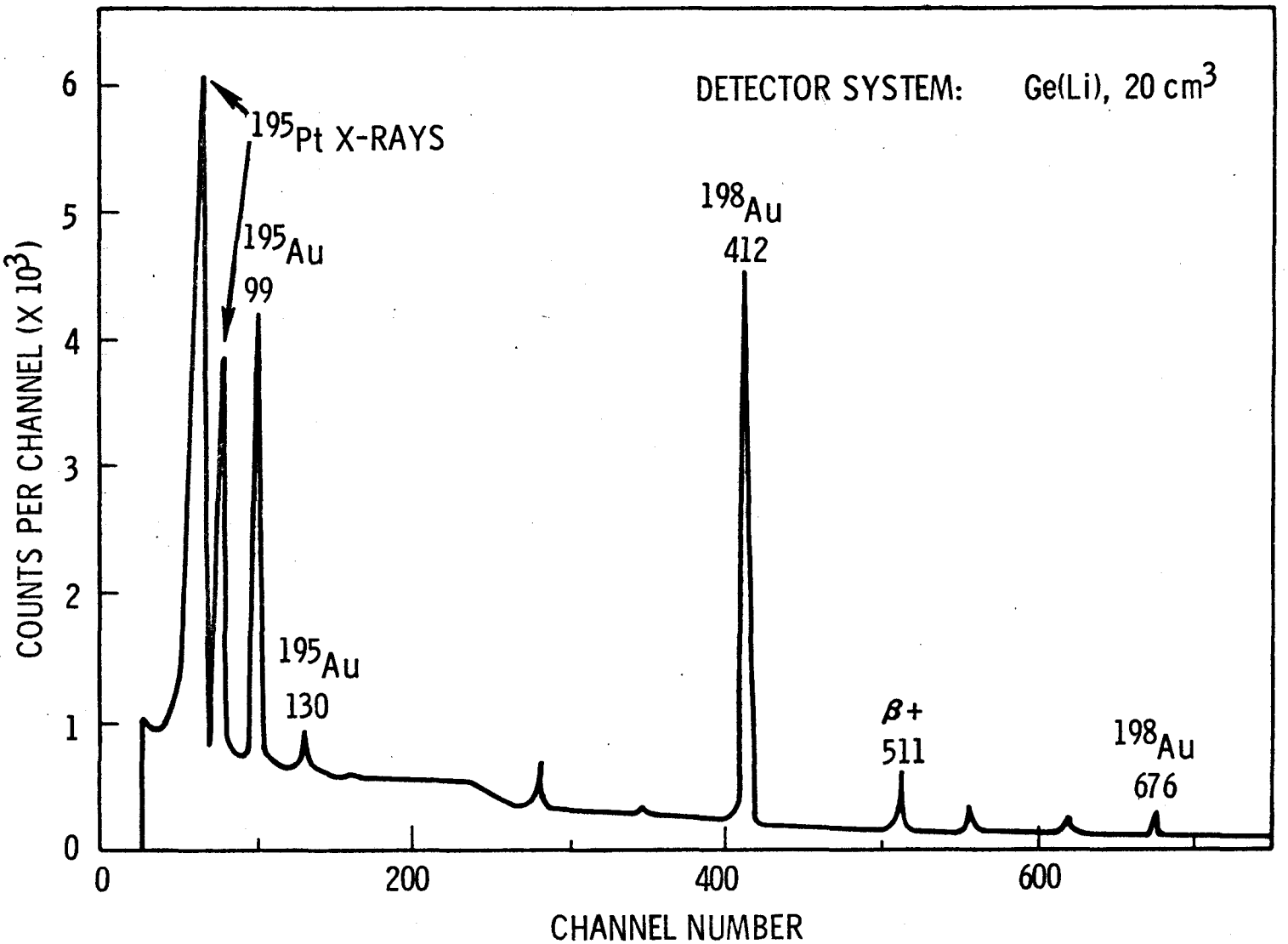

Fig. 2-17 Gamma-ray spectrum of gold-198 after chemical separation from a neutron-irradiated sediment sample.

principal oxidation state is III and has a coordination number and ionic configuration similar to gold. The positron annihilation peak is probably due to ^{24}Na.

CALCULATIONS

Chemical separation efficiencies were calculated by comparison of the ^{195}Au activity in the sample to the average ^{195}Au activity of three standards. The standards were prepared by precipitating 1 ml of the same carrier ^{195}Au solution used in the samples.

$$\text{Separation Efficiency, } E = \frac{^{195}\text{Au Activity in the sample}}{^{195}\text{Au Activity in standards}}$$

The error due to the decay of ^{195}Au for a counting time difference of two days is about 0.8%. Corrections for decay were made when the counting time difference exceeded two days. Calculations were made using the formula

$$A = Ao\ e^{-\lambda t}$$

where A and Ao are the activities of the sample at time t and time t_o, respectively. The decay constant, λ, is

$$\lambda = \frac{\ln 2}{t\ 1/2} = \frac{0.693}{t\ 1/2}$$

determined by the time required for one-half of the radioactive nuclide to decay, t 1/2, divided into the natural logarithum of 2.

Corrections for background and Compton effect were made simultaneously by subtracting from the channels in the photo-peak, an average background. This average background was determined by summing an equal

number of channels in the background on either side of the peak and dividing by the total number of channels.

The Nuclear Data, ND 2200 analyzer system, had the capability of summing a segment of the spectrum non-destructively. In practice, for a Ge(Li) diode spectrum, ten channels before the desired photo-peak were summed, ten channels which included the peak, and ten channels after. Then the sum of counts before and after the peak was averaged and subtracted from the total in the peak.

The ^{198}Au activities for a group of samples, including their respective standards and blanks, were corrected to some time, t_o. This could have been the reactor discharge time, but was usually that of the first day of counting.

The weight of gold in the sample, in nanograms (10^{-9} g), Wt (ng), was then calculated from the formula

$$Wt\ (ng) = \frac{Wts\ (ng)\ E_s}{A_s}\ \left(\frac{A}{E} - \frac{Ab}{Eb}\right)$$

where Wts is the weight of the gold in the standard in nanograms, A is the activity of the sample, and A_s and A_b are the activities of the standard and blank. E, E_s, and E_b are the separation efficiencies for the sample, standard, and blank, in that order. The blanks, and often the standards also, were averages of several values.

The values were then divided by the appropriate number of liters or grams which the sample represented to come up with conventional concentration units.

In the salt samples, standards were prepared by mixing a known amount of gold with a portion of sample material being analyzed. After

counting, the activity of the standard A_s was determined from the equation

$$A_s = A_2 - A_1 \frac{Wt_2}{Wt_1}$$

where A_1 is the activity of the sample and A_2 the activity of the standard plus sample. Wt_1 and Wt_2 are the respective weights of the samples.

These standards were compared with like amounts of gold on strips of Scotch Magic Mending tape and found to be nearly identical.

STATISTICS

1. There are two types of error, systematic and random. The practice in this study has been to compare samples to standards and to treat standards and samples alike wherever possible, thus reducing systematic errors to a minimum.
2. Random errors can be estimated by calculating the error associated with each measurement involved in determining a sample value. They can also be expressed statistically from replicate samples.
3. The reproducibility of replicate samples in this study is reported in terms of the standard deviation.

An average value of 10.8 with one standard deviation of 2.8 from a set of three replicates may be expressed $\overline{X} = 10.8 \pm 2.8$ (3) ng Au/1.

The error may also be expressed as a percent of the value. The example used above would then be expressed $\overline{X} = 10.8 \pm 26\%$ (3) ng Au/1.

The percent error usually increases as the magnitude of the value decreases for a particular method of analysis. A plot of the percent

standard deviation versus the sample value was made (Fig. 2-18). The percent standard deviation for a single value can be interpolated from the curve. For example, a value 0.1 ng Au in a 30 ml sample would have a of about 30%, and would be expressed as 3.3 $\pm$ 1.0 ng Au/1.

REPRODUCIBILITY

The amount of gold in the blank filters varied from one batch of filters to the next, but was nearly two orders of magnitude less than the samples. Reproducibility for filter replicates was for:

Standards	5.00 $\pm$ .06 (3) ng Au
Blanks	0.014 $\pm$ 0.004 (4) ng Au
Samples	1.41 $\pm$ 0.25 (2) ng Au

The ion exchange resin used for this study was all from one batch. The average gold content in the resin was 0.06 $\pm$ 0.05 (3) ng Au/g Resin. One set of resin replicates gave an average value of 2.6 $\pm$ 0.6 (3) ng Au/1, and a pair of standards had a value of 5.00 $\pm$ 0.21 ng Au.

The precision obtained in salt samples is shown in Fig. 2-18. A sample size of about 100 ml would have been more desirable. This would have reduced the standard deviation to $\leq$ 20%.

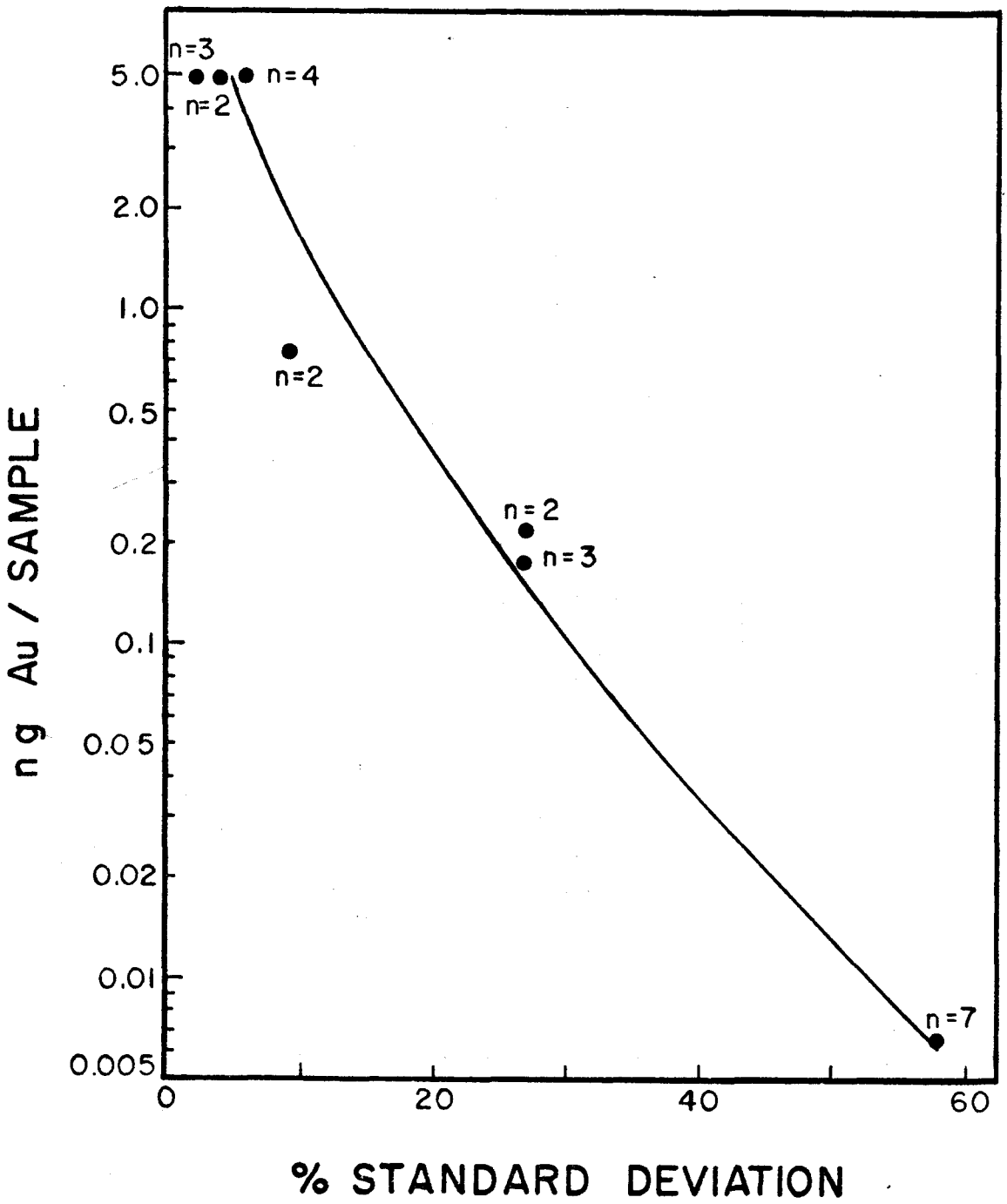

Fig. 2-18 Relationship of the error to the amount of gold in a sample.

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CHAPTER III

THE SOLUBILITY OF GOLD IN SEA WATER

INTRODUCTION

Gold, one of a group of elements referred to as noble metals, is highly resistant to aqueous solution. It is found in sea water, however, an occurrence which raises questions regarding the extent, origin and form of the gold.

Haber's (1928) value of 4 ng Au/l has been widely accepted as an average for the gold concentration in sea water. Caldwell (1938) set an upper limit for gold in Puget Sound water at 200 µg Au/l. Higher values have been reported by Stark (1943), Putnam (1953) and Hummel (1957); the maximum being approximately four orders of magnitude greater than Haber's average.

Freise (1934) reported experiments in which he attributed demonstrable transport of gold to solution by humic acids. The solution of gold by humic acids was later refuted by Fetzer (1946) and Krauskopf (1951). Cloke and Kelly (1964) demonstrated solution of gold by inorganic acid conditions which could conceivably occur in nature. Krauskopf (1951) used electromotive force values to predict that MnO_2 and possibly Fe_2O_3 and CuO would be the only metal oxides in nature able to oxidize gold. Organic matter is more apt to reduce gold rather than to oxidize it; however, organic matter may act as a transporting medium. Recent work (Morgan, 1970) in the association of sea water organics with metals indicates that some of the gold may be in the form of metal-organo complexes. Also, as suggested by Mason (1966), certain non-ionic substances (organics) may provide a protective coating for gold colloids.

Putnam (1953) was able to dissolve a gold film in a few hours in

sea water which had been enriched in ozone. Sillén (1961) used equilibrium constants published by Bjerrum (1948) to calculate a solubility for gold over three orders of magnitude of that normally found in sea water. He concluded that gold would be present primarily as $AuCl_2^-$ and that metallic gold should be unstable in contact with sea water. His calculated solubility of 12.6 µg Au/l assumed $AuCl_2^-$ to be the dominant species with a gold III concentration of 0.008 µg Au/l. The approximate percentages of possible gold III chlorohydroxy species calculated from equilibrium constants (Bjerrum, 1948) are as follows:

$AuCl_4^-$	0.01%
$AuCl_3OH^-$	1.6
$AuCl_2(OH)_2^-$	28.9
$AuCl(OH)_3^-$	43.9
$Au(OH)_4^-$	25.6

Rosenbaum *et al.* (1969) found that sea water shows a solubility of gold in sea water to be three orders of magnitude greater than that normally found in the ocean.

Gold sulfides may occur in localized areas under anoxic conditions. Manskaya and Drozdova (1968) suggest that gold would be precipitated in a sulfide media. However, gold sulfide, in low concentrations, should be quite stable (Krauskopf, 1951; Garrels and Christ, 1965).

$$AuCl_2^- + HS^- \rightleftarrows AuS^- + 2Cl^- + H^+ \qquad (3\text{-}1)$$

The solubility of gold in sea water is still in question, and more data are necessary on rates of solution. Also uncertain are the effects of a sulfide medium on the solubility of gold.

EXPERIMENTAL

An experiment was set up to approach the solubility of gold in sea water from both saturated and unsaturated solutions. Gulf of Alaska sea water (Cl $^{o}/_{oo}$ = 18) was used to make up a series of solutions. Water for solutions A and D (Fig. 3-1) was passed through a 0.01 μ HA Millipore filter and oxidized with persulfate similar to a method described by Slowey (1966). Sea water was refluxed for 5 min. after the addition of 10 ml 0.1N $K_2S_2O_8$ and 10 ml 0.4N HCl per liter. The solution with all of the gold in the III oxidation state was passed through a column of BIO-RAD AG-1-X8, 100-200 mesh strong-anion exchange resin, to obtain gold-free sea water.

Fifty milligrams of metallic gold tagged with ^{195}Au was added to one liter of solution A. The tagged metallic gold was prepared by mixing ca 16 μCi ^{195}Au with native gold as $AuCl_4^-$ in 50 ml of 2N HCl. The gold was precipitated with 10 ml of 5% hydroquinone and the precipitate was boiled for 20 min. to coagulate the gold. The clumps of gold were filtered, washed with hot water and ethyl alcohol, then heated to 500°C in a muffle furnace to insure destruction of all organic matter. The activity was 455 c/min/μg Au. At least 10,000 counts were obtained for all measurements of the radioactive tracer including the background. This gave a relative standard deviation of 1%.

Soluble gold, a mixture of ^{195}Au and native gold prepared as above, was added to solution D and diluted to one liter. The initial concentration was 100 μg Au/l with an activity of 106, 440 c/min/μg Au.

Water for solution B was passed through a 0.45 μ HA Millipore

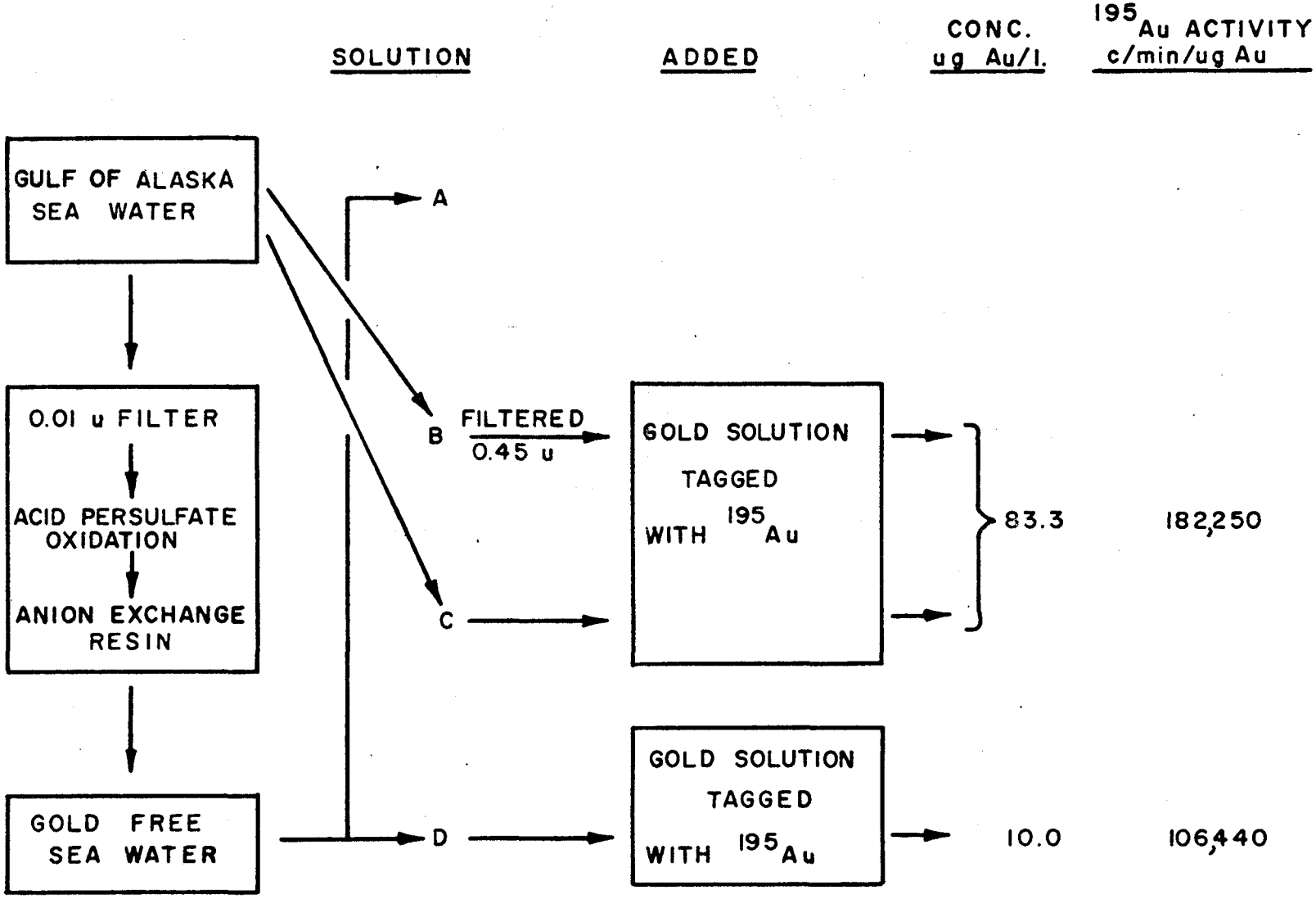

Fig. 3-1 Scheme for preparation of solutions to determine the solubility of gold in sea water.

filter. Solution C was unfiltered (Fig. 3-1).

A mixture of ^{195}Au and native gold in solution as $AuCl_4^-$ was added to solutions B and C. The final concentration was 83.3 µg Au/l with an activity of 182, 250 c/min/µg Au. The gold originally present was insignificant compared to the amount added. The pH of all solutions was adjusted to 8.0 ± 0.2.

The solutions were contained in Pyrex glass-stoppered bottles which had been thoroughly cleansed with hot aqua regia. The solutions were stirred 2 to 3 hours daily with the aid of magnetic stirrers using Teflon-coated stirring bars. The bottles were insulated from the stirring motors to maintain the temperature at 23 ± 1°C.

RESULTS

The results are shown in Fig. 3-2. The final concentration of solutions B and C were 6.6 and 7.3 µg Au/l, respectively. It was found that centrifuging portions of solutions B and C removed approximately 45% of the activity (2500 rpm for 20 minutes in polypropylene centrifuge tubes, International Clinical Centrifuge Model CL). This reduced the actual soluble gold to about 4.0 µg Au/l. Nearly all of this activity (96%) was retained on the strong anion exchange resin, indicating an ionic species of gold was present.

Of particular interest is the relatively rapid dissolution and approach to equilibrium of gold in solution A. It appears that a solubility of ca 4 µg Au/l can be expected for the conditions stated.

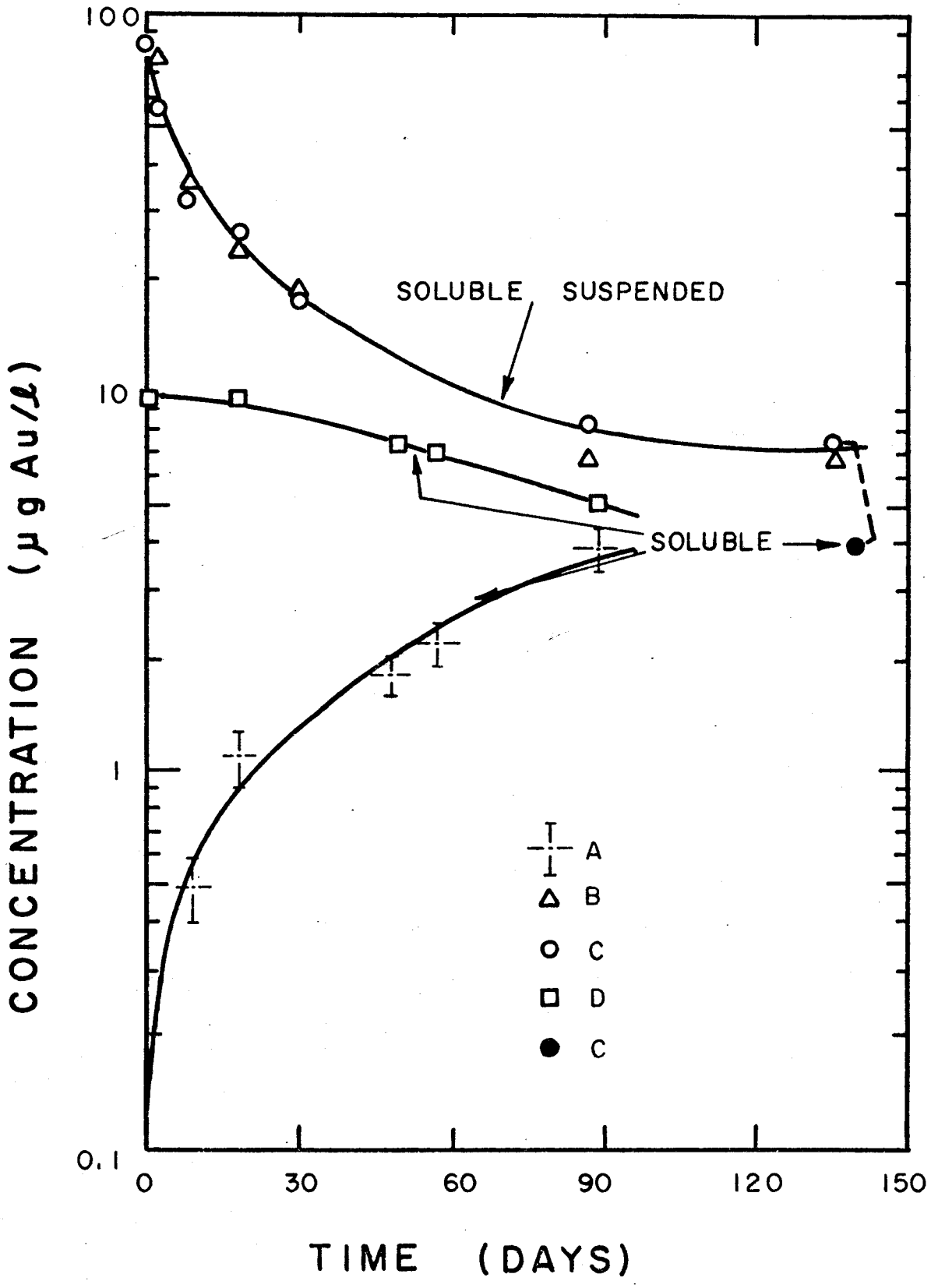

Fig. 3-2 Change in concentration of gold in sea water solutions with time. C (soluble) ● is the concentration of gold in the final C solution after centrifugation.

GOLD IN SEA WATER CONTAINING SULFIDE

Ten milliliters of solution D which had been centrifuged were mixed with an equal amount of sulfide containing sea water (pH = 8) which had also been centrifuged. The final concentration of sulfide was near 300 µg-at. $S^{=}$/l, similar to that found in some natural systems (Richards et al., 1965). No noticeable change occurred. The solution was stored in a screw-cap pyrex bottle for 24 hours; a portion of the solution was then centrifuged. No reduction in the ^{195}Au activity was detected. The solution was then passed through a column of BIO-RAD AG-1, with 93% retention. The effluent was acidified and passed through a fresh column, with another 5% retained. Approximately 2% of the gold remained in solution. The experiment was repeated after two weeks with no significant change observed.

CONCLUSIONS

Gold dissolves in sea water under laboratory conditions to near equilibrium in a matter of months. The solubility found was on the order of 4 µg Au/l for sea water of Cl = 18 °/₀₀ at 23 ± 1°C. This is three orders of magnitude higher than usually found and on the same order as many of the highest values reported in recent literature. The oceans should have reached equilibrium with gold because of the exposure of sea water to beach sands and marine sediments input from the land through geologic time.

Therefore it appears that there are chemical factors controlling gold concentrations at a low level. Gold concentrations are not lower in

sulfide environments, since gold sulfide complexes are soluble in sea water. Low gold concentrations are probably a result of scavenging by biological organisms, clay sized particles, high molecular weight organic matter and hydrolyzate sediments.

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CHAPTER IV

DETERMINATION OF GOLD IN GEOLOGICAL MATERIALS BY NEUTRON ACTIVATION ANALYSIS

INTRODUCTION

Gastineau Channel separates Douglas Island from the mainland in southeastern Alaska (Fig. 4-1). The channel runs southeast from Juneau emptying into Stephens Passage. The two highest producing gold mines of the one-hundred-mile-long Juneau gold belt, the Alaska-Juneau and Alaska-Treadwell mines are located near Juneau (Fig. 4-2). Run-off from these and lesser gold-bearing areas drain into Gastineau Channel.

The Juneau gold belt lies between the Coast Range diorite batholith core to the east, and greenstone chloritic schists to the west (U.S. Bureau of Mines, 1967). Wide lodes, containing low-grade stringers running parallel to the foliation of the schistose or slaty country rock, are the most productive (U.S. Senate, 1964). The gold at the Alaska-Juneau mine is in irregular quartz stringers and gash veins in slate and metagabbro which intrude metamorphosed sedimentary rocks. At the Alaska-Treadwell mine, the gold is evenly distributed in mineralized albite-diorite dikes which intrude a structure of black slate. An excellent account of gold mining activity in the Juneau gold belt is given by Spencer (1906). Locations of mines in the Gold Creek area are shown in Fig. 4-3.

In general, gold placer deposits are found within a few kilometers of the gold source and the mean particle size decreases with distance from the source (U.S. Senate, 1964). Gastineau Channel is a logical location to find marine gold deposits. An evaluation of the potential of this area as a gold source would require a knowledge of the concentration and distribution of gold and the size distribution of the sediment.

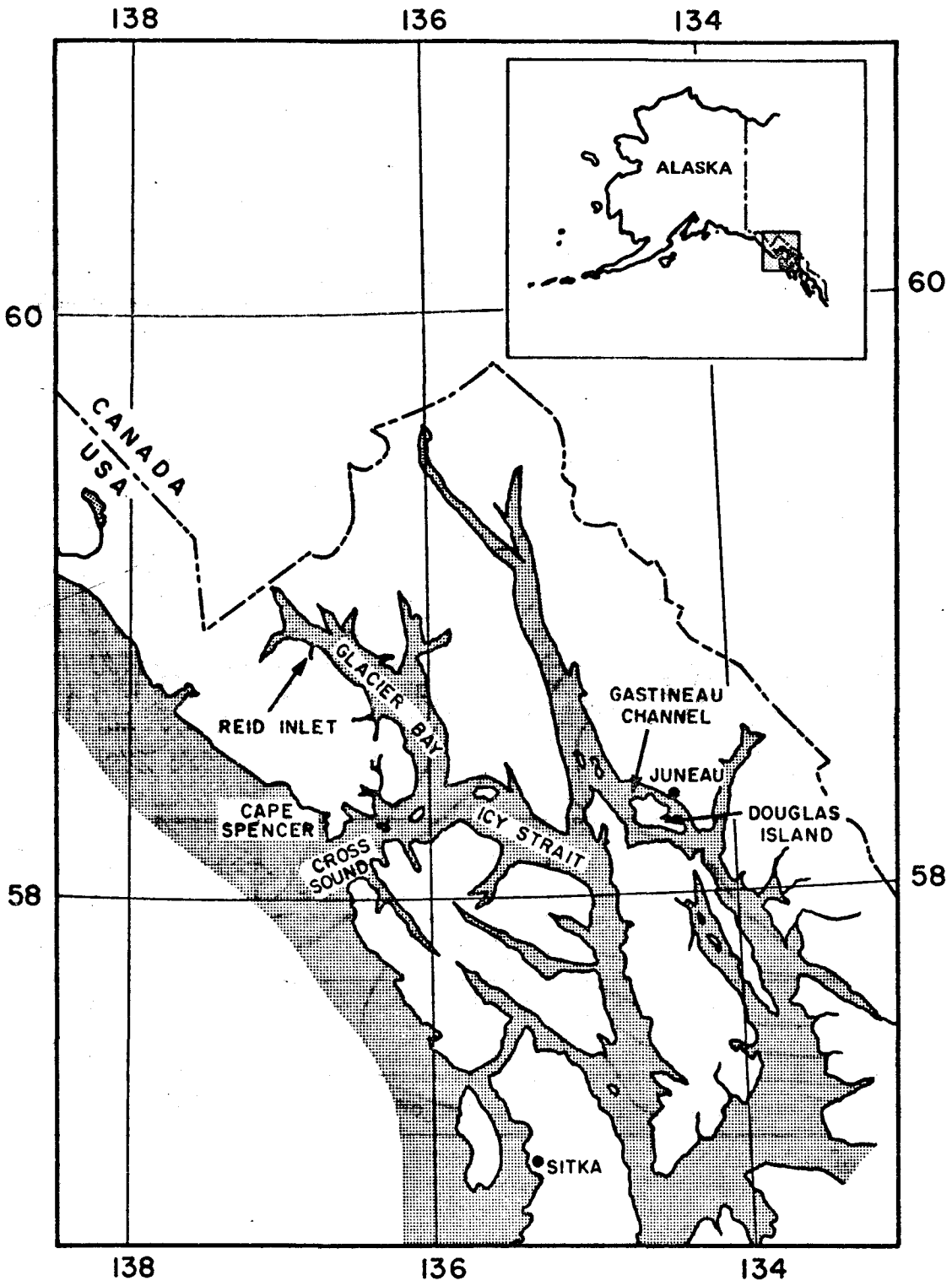

Fig. 4-1 Map of southeastern Alaska showing general location of Gastineau Channel and Juneau.

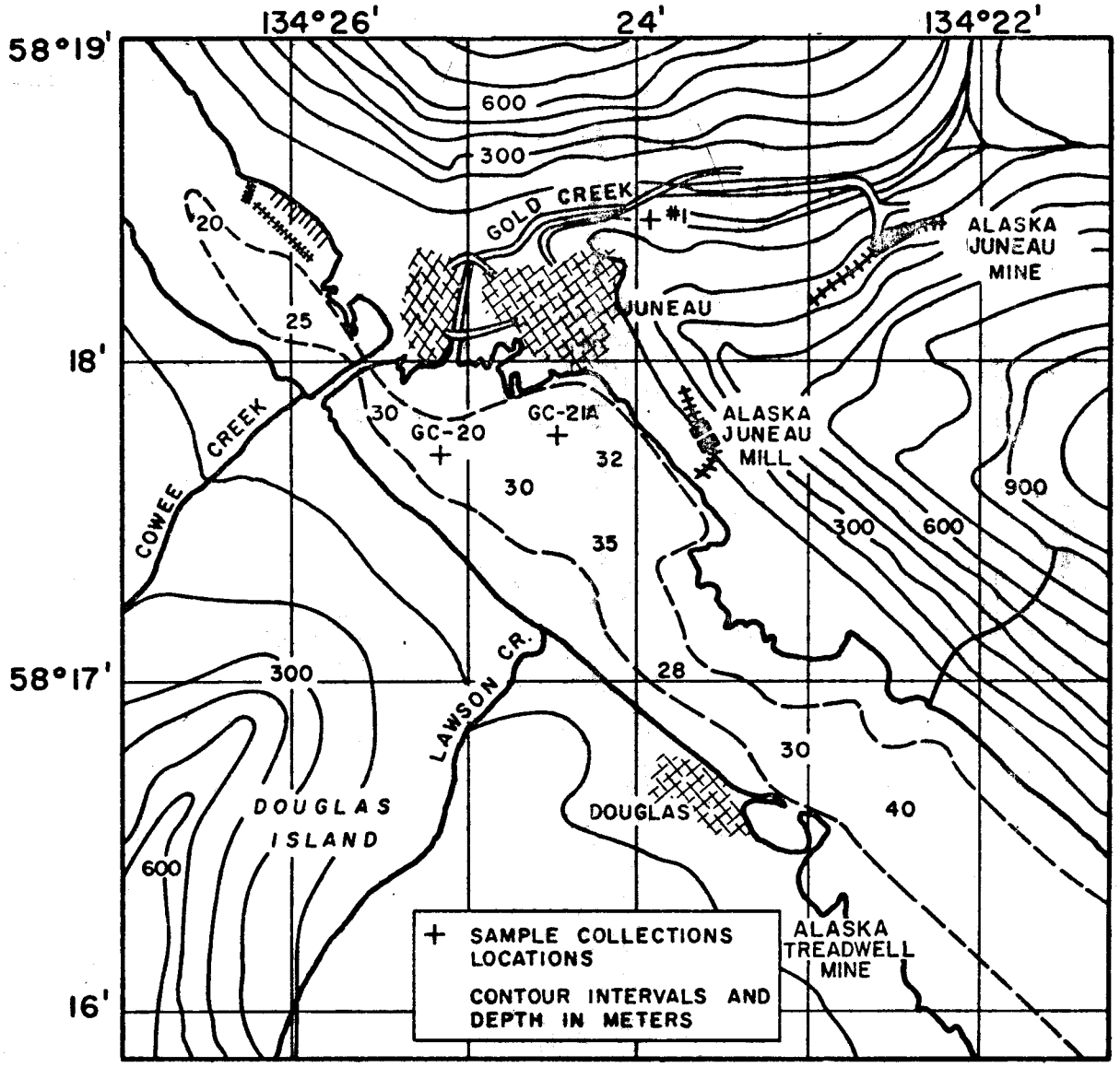

Fig. 4-2 Location of Gastineau Channel stations and Gold Creek where samples were obtained. Major gold mines in the Juneau-Douglas area are also shown.

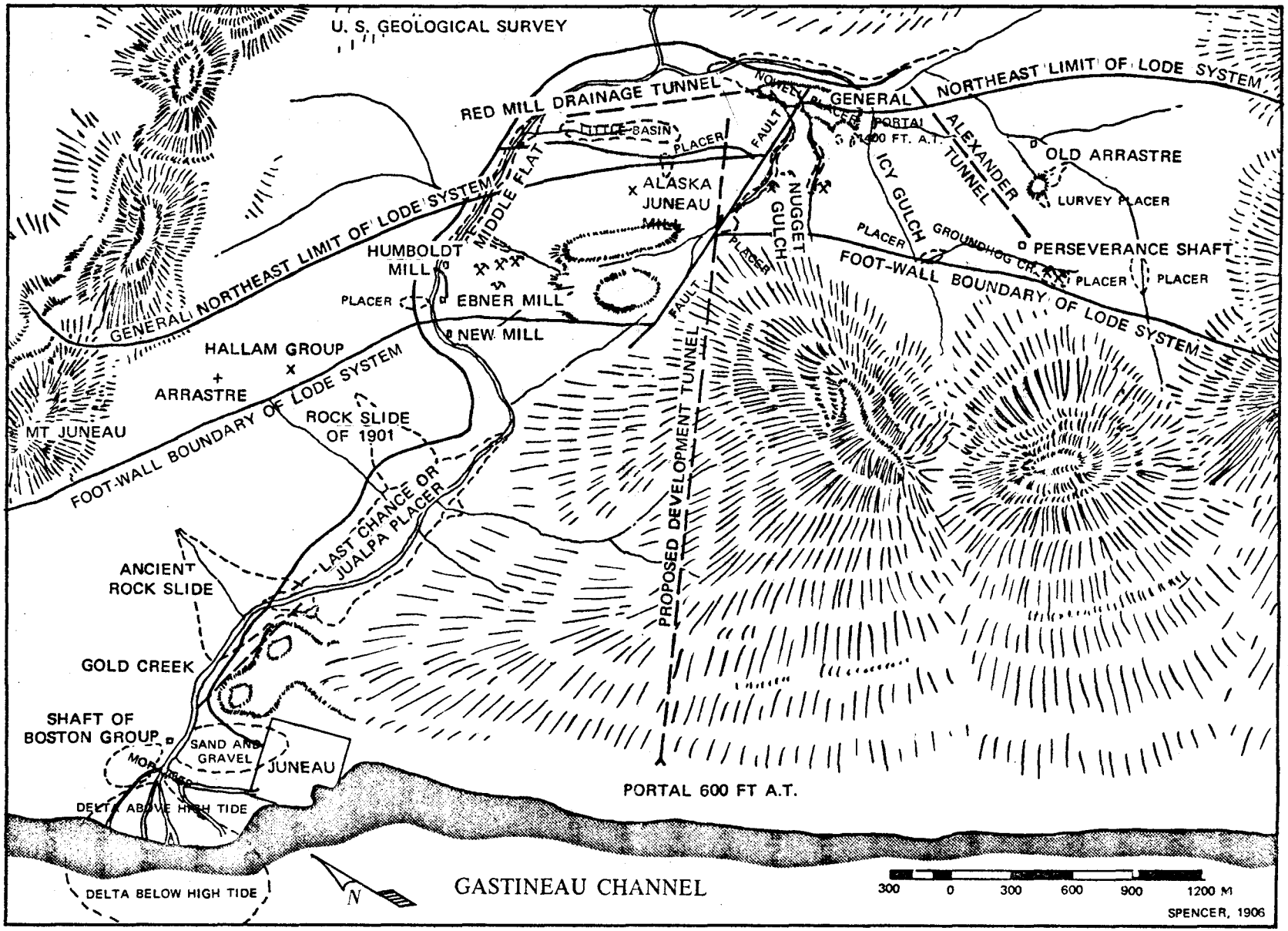

Fig. 4-3 Map of Gold Creek area showing position of mines and extent of lode system (1906).

Neutron activation analysis, NAA, was chosen for this study because of the sensitivity available (sub-parts per trillion). Native gold, element number 79, is 100 per cent ^{197}Au, with a relatively high capture cross-section for thermal neutrons, 96 barns (Lederer et al., 1967). The interaction of thermal neutrons with ^{197}Au produces ^{198}Au, which decays with a half-life of 2.7 days by beta emission to ^{198}Hg. The amount of gold present in a sample can be determined by comparison of the 412 KeV photo-peak area of the sample with that of a gold standard. NAA has been used successfully for detecting gold in geological materials by a number of investigators and is especially well-suited for samples with low gold content. Goldberg and Brown (1950) used NAA to determine the amount of gold in meteorites. Shcherbakov and Perezhogin (1963, 1964) analyzed a large variety of geological materials by NAA. Gold concentrations in marine sediments, determined by NAA, were reported by Crocket et al. (1968), and Harriss et al. (1968).

EXPERIMENTAL

Sampling

A preliminary investigation of the Juneau area was made by collecting samples from Gold Creek and Gastineau Channel in April, 1969 (ACONA Cruise 089). A hand sample from the Gold Creek stream bed was obtained by randomly collecting ten portions of sediment totalling about 1 kg. The area sampled was between the City of Juneau and the Alaska-Juneau Mine (Marked "#1" in Fig. 4-2). Sediment was obtained from Stations GC-20 and GC-21A (Fig. 4-2) with a Shipek grab. The sediment was removed

from the interior of the grab sample so as to avoid possible contamination from the sampling apparatus. A nylon spatula was used in transferring the sample to polyethylene bags.

The samples were each thoroughly mixed and divided to obtain two splits of about 100 g from each sample. The samples were dried to constant weight at 120°C, then sieved through stainless steel screens. The cumulative weight percent for the averages of each sample is shown plotted against screen size expressed in phi (ϕ) units (Fig. 4-4). There is a great similarity between the curves for Gold Creek and GC-20. The discrepancy lies mainly in the lack of fines in the creek sediment. The fine sediment GC-21A exhibited a blackish-green color indicating the presence of organic mater.

Preparation of Samples for Analysis

Contamination is an ever-present factor in trace element analysis. A very good discussion of the control of contamination is given by Thiers (1957) and more specifically related to the marine studies, by Schutz (1964) and by Robertson (1968). The conclusions of these and other authors were taken into consideration in this study to reduce contamination to a minimum.

Samples were sealed in polyethylene capsules, as were appropriate standards. Most of the sample preparation was done in an Agnew-Higgins laminar-flow clean hood located in a room used only for sample preparation. Polyethylene gloves were worn while handling samples, all metallic objects were coated with vinyl paint, and all glassware was cleaned with hot aqua regia.

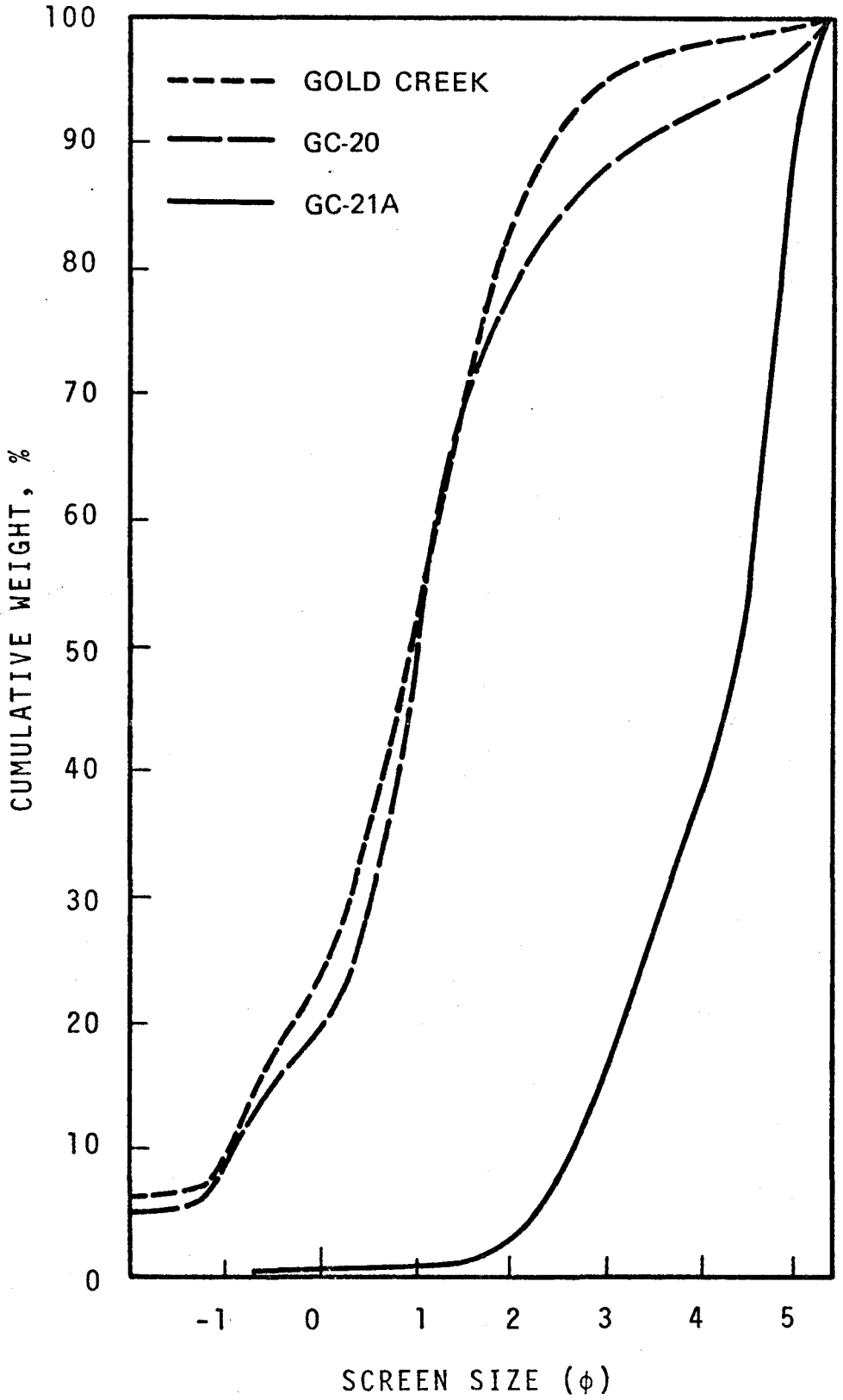

Fig. 4-4 Cumulative weight percent as a function of screen size (ϕ), of the sediment samples.

Standards were prepared by adding 50 µl of a gold chloride solution, 10^{-7} g Au/ml, to a sediment matrix, or on clear plastic tape. Standards were treated the same as samples.

The individual sample capsules were heat-sealed, then placed in polyethylene capsules approximately 4.5 cm inside diameter and 7.3 cm overall length. The tops were then heat-sealed. Depending upon the type of sample capsules used, two or three tiers of capsules were combined in each large capsule.

Irradiation

The samples were irradiated with thermal neutrons in a U.S. Atomic Energy Commission graphite production reactor at the Hanford Site, near Richland, Washington. The integrated flux received by the samples was about 1.5×10^{18} n cm^{-2}. Cooling periods of 2 to 6 days allowed short-lived activities to decay sufficiently for safe handling.

Geological materials were analyzed by two different procedures.

First Method

1. The irradiated 100 mg sample was emptied into a 50 ml nickel crucible.
2. One milliliter of the gold carrier - ^{195}Au solution was added and heated to reduce the gold. (The radioactive ^{195}Au was added to the gold carrier to check the separation efficiencies in lieu of weighing similar to a procedure reported by Green et al. (1969).
3. One to two grams of sodium peroxide was added and the crucible heated to a dull red (650°C) for about 30 min (Suttle et al., 1969). (A note of caution - the crucible begins to lose its integrity at about 700°C).
4. The crucible was then quenched in cold water.

5. The fused mixture was transferred from the crucible with water into a 250 ml beaker and acidified with conc. HCl to dissolve the fused material.

6. The gold chloride was extracted from the acid solution with 30 ml of ethyl acetate following the procedure of Goldberg and Brown (1950). The extraction process was carried out immediately after acidification of the fused mixture and before silica gel began to form.

7. The aqueous phase was drained off and retained. The acetate phase was washed twice with 20 ml of 1N HCl. The washings were added to the initial aqueous phase.

8. The aqueous phase was then extracted with ethyl acetate twice more. The washings were discarded as was the final aqueous phase.

9. The ethyl acetate phases were combined in a 100 ml beaker and dried under an infrared lamp.

10. The gold chloride was dissolved in 20 ml of 2N HCl and brought to a boil.

11. Ten milliliters of 5% aqueous solution of hydroquinone were added and boiling continued for about 20 min to coagulate the precipitated gold.

12. The precipitated gold was filtered in a chimney filter apparatus onto a 25 mm diameter filter, washed with two 25 ml portions of hot water, placed on a 25 mm counting planchet, and dried under an infrared lamp.

13. The filter was dissolved with a few drops of acetone, dried, and double-wrapped with plastic wrap for counting. Chemical yield for the process was about 90%.

The separation scheme is shown in Fig. 4-5.

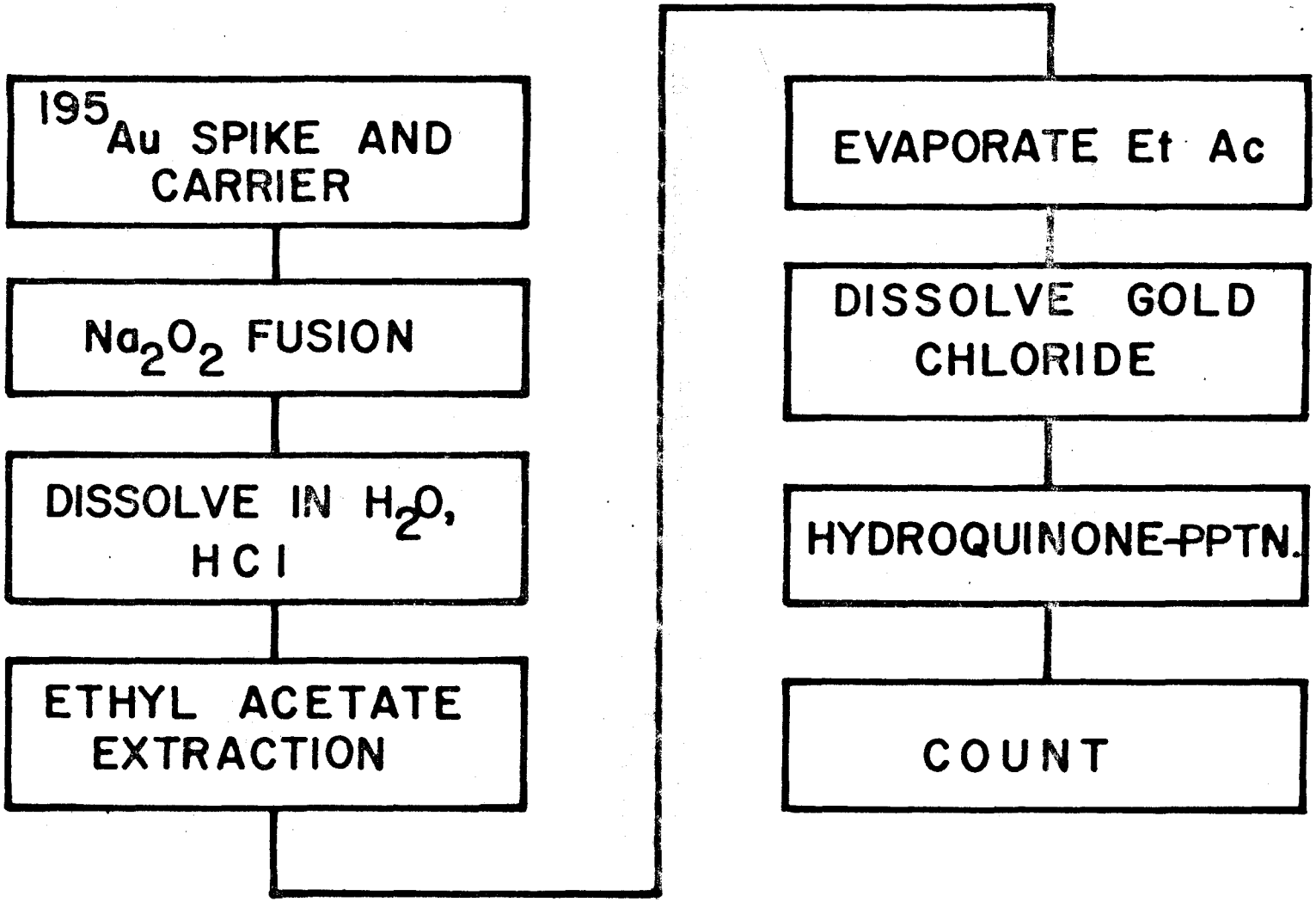

Fig. 4-5 Chemical separation scheme for first method.

Counting Procedures

The photopeak magnitude of the gold isotopes, ^{195}Au and ^{198}Au, 99 KeV and 412 KeV, respectively, were measured by counting the samples with a Ge(Li) solid state detector-multichannel analyzer system. The samples were counted long enough to obtain at least 10,000 counts in most cases. Samples of low gold content were counted for a maximum of 10 hours on the Ge(Li) diode detector and then an appropriate amount of time using a 7.6 x 7.6 cm NaI(Tl) detector. Standards were counted with each group of samples in the same geometry. Most samples could be counted in 1 to 2 hours.

Instrumentation

A 20 cm^3 Nuclear Diodes Ge(Li) diode detector was used in the study in conjunction with a Nuclear Diode Model 101A pre-amplifier and a Tennelec Model TC 202 BLR Linear amplifier. The signal was fed into a Nuclear Data ND 2200/4096 channel analyzer. The photopeak of the 1.332 MeV gamma of ^{60}Co was about 3.5 percent of that obtained using a 7.6 cm x 7.6 cm NaI(Tl) detector at a distance of 25 cm. The peak to Compton ratio was about 16.5 and the resolution was 2.6 KeV FWHM for the 1.332 MeV photopeak. The detector was mounted vertically and shielded in a cave with 10.2 cm thick walls. The advantages of Ge(Li) solid state spectrometry over NaI(Tl) for resolution have been well documented (Cooper et al., 1968; Robertson et al., 1968; Funk et al., 1969).

Gamma-ray Spectrum

A typical sample spectrum is shown in Fig. 4-6. The 99 KeV photopeak of ^{195}Au was measured as the radiochemical separation monitor.

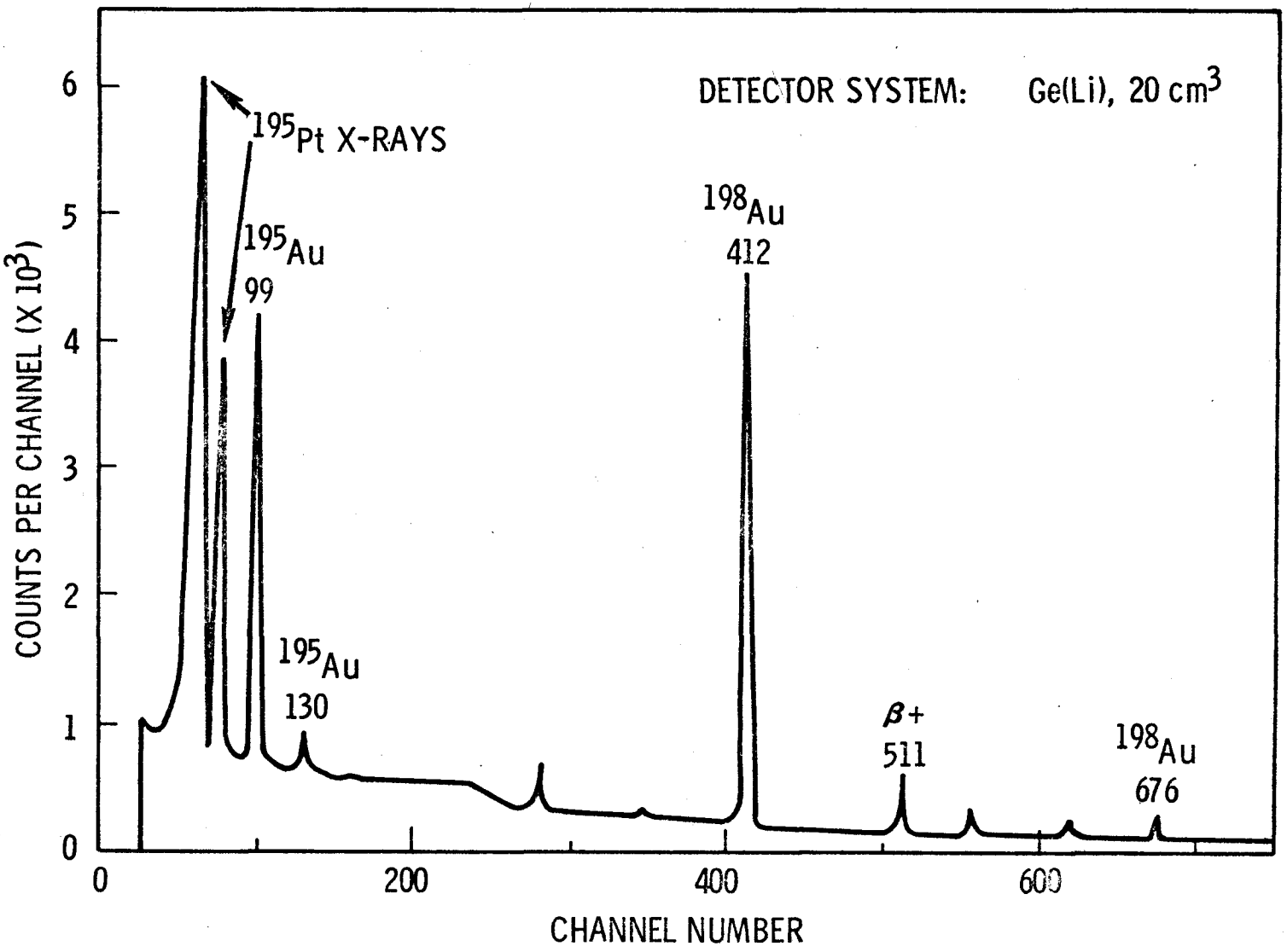

Fig. 4-6 Gamma-ray spectrum of gold-198 after chemical separation from a neutron-irradiated sediment sample.

The amount of gold in the sample was determined by comparison of the 412 KeV ^{198}Au photopeak area with that of a gold standard.

Calculations

Chemical separation efficiencies, E, were calculated by comparison of the ^{195}Au activity in the sample to the average ^{195}Au activity of three standards.

The standards were prepared by precipitating 1 ml of the same carrier ^{195}Au solution used in the samples for the first method, or by pipetting ^{195}Au solution into polyethylene capsules for the second method. The error due to the decay of ^{195}Au for a counting time difference of two days is about 0.8 percent. Corrections for decay were made when the counting time difference exceeded two days. Corrections for background and Compton effect were made simultaneously by subtracting an averaged background from the channels in the photopeak. The total peak area method of determining the activity was used.

The Nuclear Data ND2200 analyzer system used had the capability of summing a segment of the spectrum non-destructively. In practice, an equal number of channels before and after the desired photopeak were summed and averaged. The background was then subtracted from the total counts in a like number of channels which included the photopeak.

The weight of gold in the sample, Wt, in micrograms, was then calculated from the formula

$$Wt = Wt_s \frac{A}{A_s} \frac{E_s}{E}$$

where Wt_s is the weight of the gold in the standard in micrograms, A is the activity of the sample, and A_s is the activity of the standard. E

and E_s are the separation efficiencies for the sample and the standard, respectively.

Standards were prepared by mixing a known amount of gold with a portion of sample material being analyzed. After counting, the activity of the standard A_s was determined from the equation

$$A_3 = A_2 - A_1 \frac{Wt_2}{Wt_1}$$

where A_1 is the activity of the sample and A_2 the activity of the standard plus sample. Wt_1 and Wt_2 are the respective weight of the samples. These standards were compared with like amounts of gold on strips of clear plastic tape and found to be nearly identical.

Errors

1. Systematic errors were minimized by direct comparison to standards treated as samples. Random errors can be estimated by calculating the error associated with each measurement involved in determining a sample value. They can also be expressed statistically from replicate samples. The reproducibility of replicate samples in this study is reported in terms of the standard deviation with the number of replicates in parenthesis.

It was found that due to the inhomogeneous distribution of gold in geological materials the reproducibility in such small samples was poor. USGS standard rock, W-1, was analyzed for gold by the first method in triplicate with a standard deviation of 18 percent. An average value of 4.5 ± 0.8 (3) ppb was obtained. This compares with 5.0 ppb gold in W-1 given as an average from data accumulated by Fleischer (1965) and 4.6 ± 0.8 (8) ppb from analyses performed by Fritze and Robertson (1969).

Clifton et al. (1967) found poor precision in the analysis of gold in up to 2 grams of raw samples of well-sorted beach sands. They found that greatly improved reproducibility was obtained by first sieving the samples.

Irradiating gram-sized samples is undesirable because of the large amounts of radioactivity produced. A second procedure was developed to handle larger samples.

Second Method

1. Ten grams of sediment were placed in a 100 ml nickel crucible and about 0.05 μCi of ^{195}Au were added.
2. The sediment was thoroughly mixed with sodium peroxide and then covered with a 0.5 cm layer of sodium peroxide, allowing about 1 cm free space in the top of the crucible.
3. The crucible was then heated to 650°C for 30 min in a muffle furnace.
4. The fused mixture was quenched in cold water and removed with triple-distilled water into a 400 ml beaker. The mixture was acidified with concentrated HCl just to the point where a clear green ($NiCl_2$) solution resulted.
5. Fifty ml of re-distilled ethyl acetate were used to extract the gold chloride. The aqueous phase was retained for re-extraction and the acetate phase was washed twice with 30 ml of 1N HCl.
6. A second and third extraction of the gold chloride from the aqueous phase was performed with 30 ml of ethyl acetate. Each acetate phase was washed with dilute HCl as in Step 5.
7. The acetate phases were combined and concentrated by evaporation. The concentrate was transferred to a 2/5 dram polyethylene snap-top

vial and dried under an infrared lamp.

8. The vial was then irradiated with thermal neutrons. After a cooling period of several days the gold chloride was dissolved in a few drops of ethyl acetate and transferred to a clean polyethylene vial for counting.

The separation scheme is shown in Fig. 4-7.

One set of the six finest sediment sizes from each location sampled was analyzed for gold by the second method.

RESULTS

The analytical results for gold in the sieve fractions is summarized in Table 4-1 along with the sediment sizing data. Triplicate analysis of the pan fraction from station GC-21A gave a value of 0.162 $\pm$ 0.012(3) ppm, an error of about 7 percent. Some of the sample sieve fractions were insufficient to provide meaningful results (GA-21A, > 0.5 mm). The error in the gold concentration associated with sub-samples less than 2 g is on the order of 50 percent (Gold Creek, < 0.038 mm). The average gold concentration in the total sample was 0.104 $\pm$ 0.004 ppm for all three locations. This value was calculated by summing the gold in each fraction and estimating the amount of gold in the fractions not analyzed (< 5%).

DISCUSSION

A plot of gold concentration as a function of screen size (Fig. 4-8) shows a predominance of gold in the 4 ϕ size (0.062-0.124 mm) for Gold Creek sediment and for the Gastineau Channel sediment just off

Table 4-1. Splitting fraction data for Gold Creek and Gastineau Channel.

Screen			Sediment		Gold	
Mesh	mm	ϕ	Weight %	Cum. Wt. %	Weight µg Au/g Sediment	
Gold Creek, Juneau, Alaska, Hand Sample						
8	2.38	-1.19	7.39	7.39		
12	1.41	-0.705	8.15	15.15		
16	1.000	0	9.02	24.55		
32	0.500	1	27.98	52.53	0.024	
60	0.250	2	30.48	83.01	0.122	
115	0.125	3	12.41	94.55	0.088	
250	0.062	4	2.79	98.21	1.49	
400	0.038	4.64	0.84	99.04	0.257	
Pan		<4.64	0.86	99.90	0.077	
GC-20, Grab						
8	2.38	-1.19	6.56	6.56		
12	1.41	-0.705	6.78	13.34		
16	1.000	0	6.31	19.64		
32	0.500	1	28.07	47.71	0.013	
60	0.250	2	30.47	78.17	0.032	
115	0.125	3	10.29	88.46	0.020	
250	0.062	4	4.08	92.54	1.78	
400	0.048	4.64	2.18	94.72	0.083	
Pan		<4.64	4.93	99.65	0.151	
GC-21A, Grab						
16	1.000	0	0.25	0.25		
32	0.500	1	0.26	0.50		
60	0.250	2	1.79	2.29	0.068	
115	0.125	3	14.87	17.16	0.032	
250	0.062	4	21.24	38.40	0.079	
400	0.038	4.64	17.43	55.83	0.090	
Pan		4.64	43.85	99.67	0.162 ± 0.012(3) 7.4%	

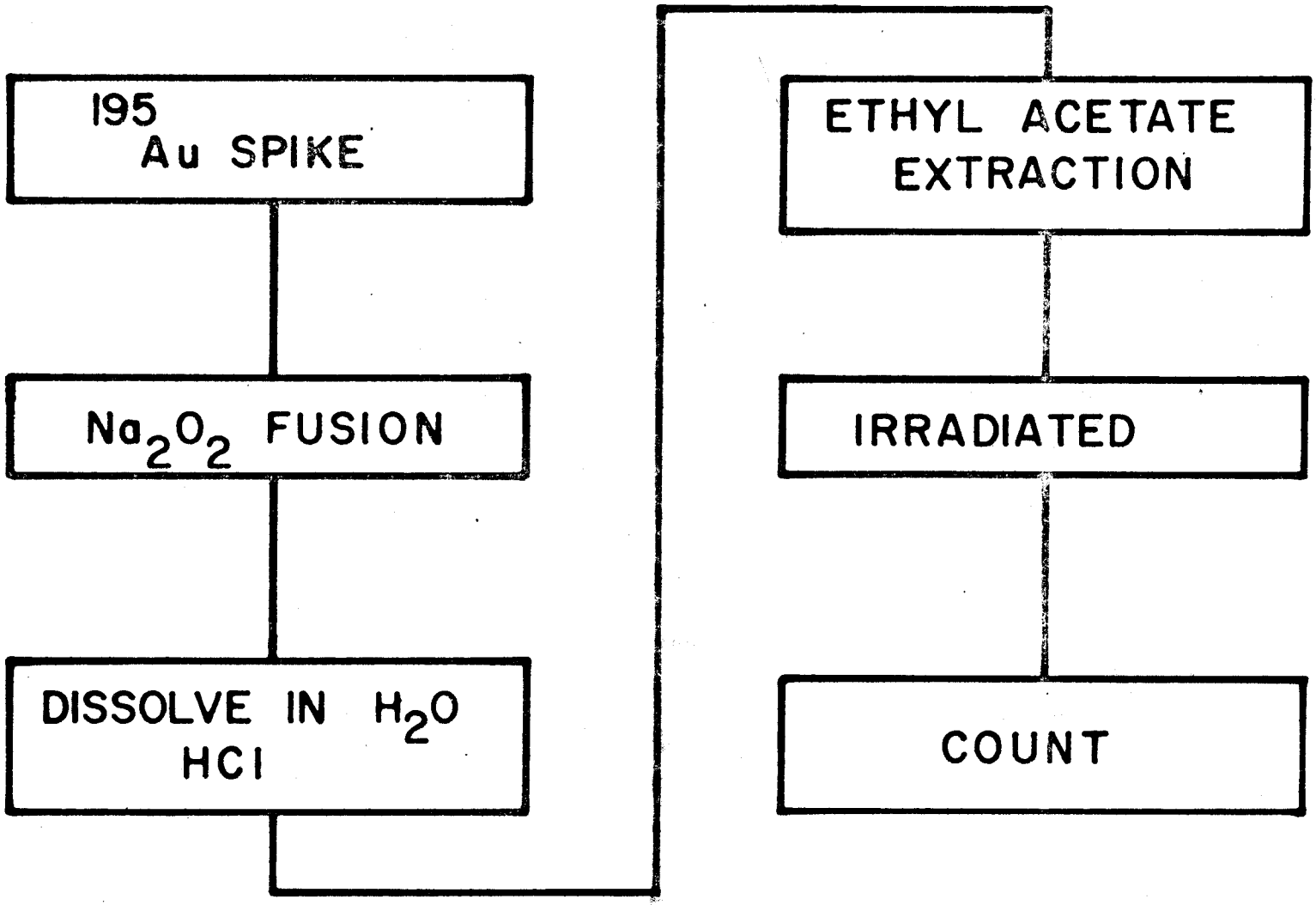

Fig. 4-7 Chemical separation scheme for the second method.

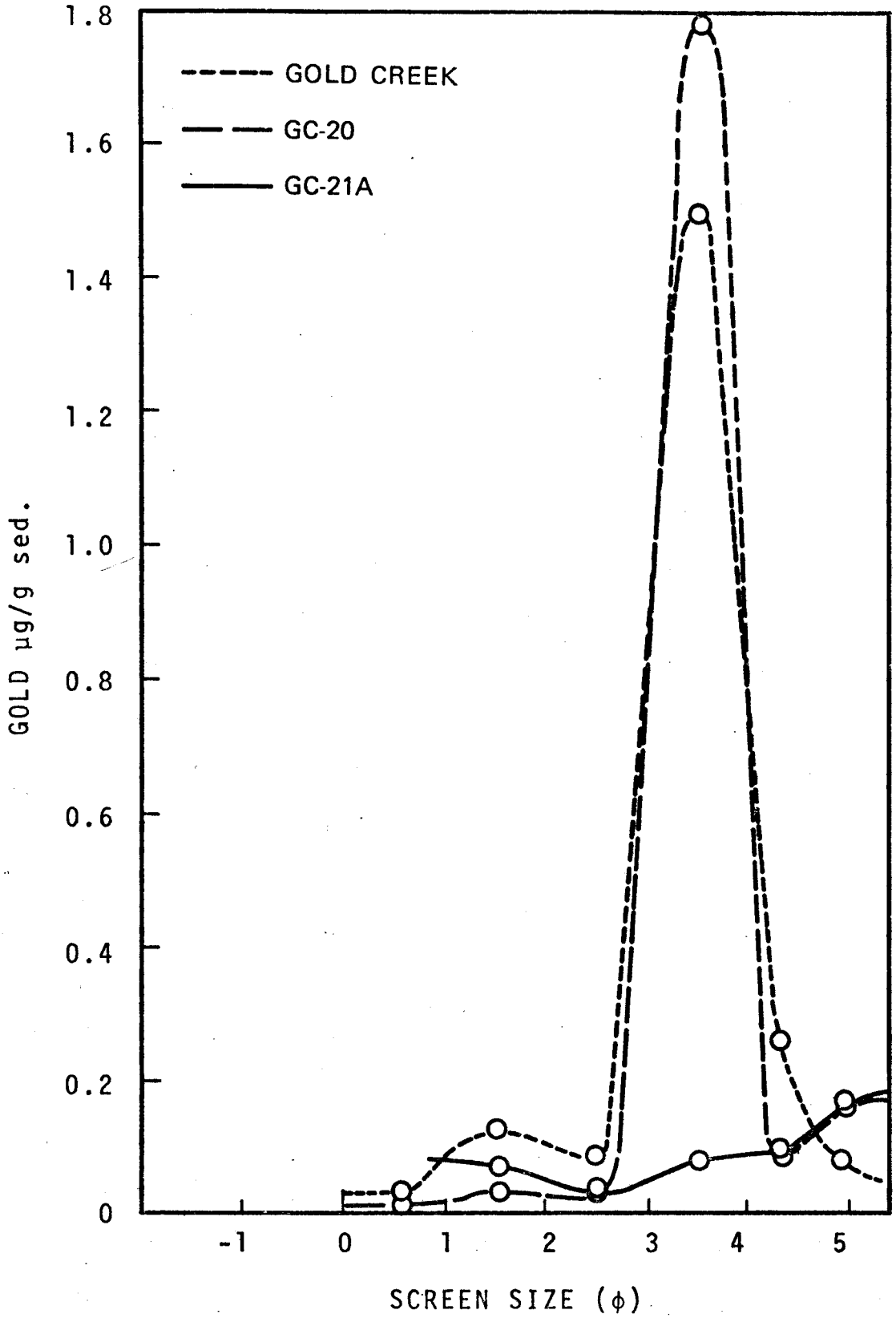

Fig. 4-8 Concentration of gold as a function of screen size (ϕ) of sediment samples.

the Gold Creek delta. The concentration of gold in the fractions of GC-21A sediment generally increases with decreasing grain size. This would be expected for a station further removed from the source than GC-20 and in less turbulent water. A decrease in the gold content of the 2 ϕ fraction of the marine sediments relative to the Gold Creek sediment was noted. This was accompanied by an increase in the gold content of the fines or pan fraction of the marine sediments over the Gold Creek fines.

A comparison of the weight percent of the sediment and of the gold as a function of screen size for the three locations is shown in Fig. 4-9. A definite bi-modal gold distribution existed in the Gold Creek sample with the lower ϕ size gold mode coinciding with the sediment mode. The gold distribution in the GC-20 sample was tri-modal with a definite shift from the 2 ϕ to the 4 ϕ mode and an increase in the pan mode.

The trend of gold content, increasing with ϕ as the distance from the source increased, can clearly be seen in the GC-21A sample.

It would appear that the gold particles decreased in size as they were transported into the marine environment, since the average concentration of gold in the sediment remains nearly constant. This could be the result of abrasion or solution. However the distribution can also be explained more plausibly by the tendency for fine sediment to be transported more readily and further than coarse sediment. Gold is fairly resistant to both mechanical and chemical attack, as demonstrated by the fact that the concentration of gold in the pan fraction of the GC-21A sample had not increased over the same fraction in the GC-20 sample.

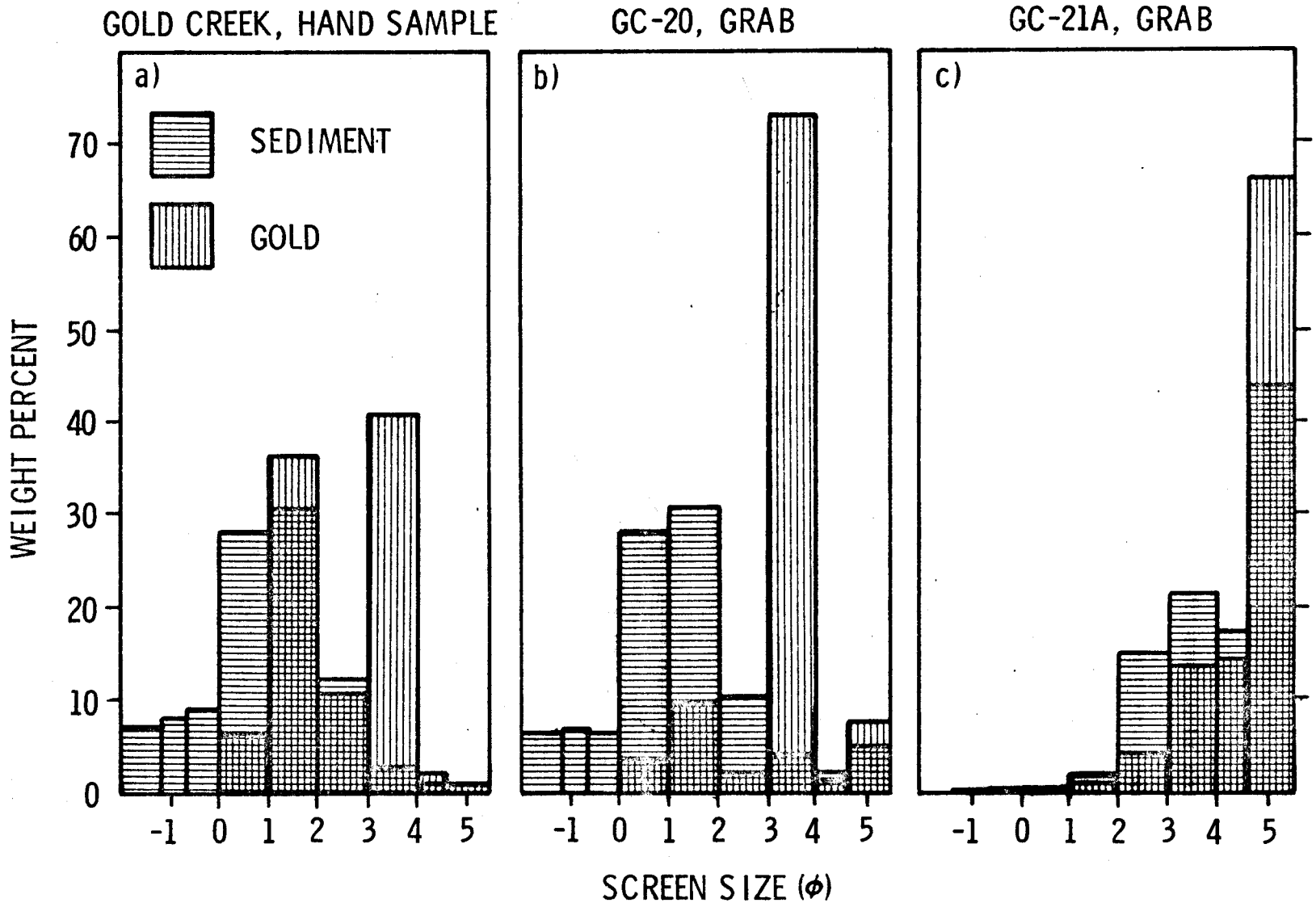

Fig. 4-9. Histogram of weight percent of sediment and gold as a function of screen size (ϕ) for sediment samples analyzed.

CONCLUSIONS

Accurate and precise gold concentrations in sediments can be determined using neutron activation analysis after pre-extracting the gold from 10 g sub-samples. The results clearly indicate trends of gold distribution in sediments transported into the marine environment. Transport mechanisms appear to be entirely mechanical in this environment, with no chemical influences detectable.

The concentration of gold in the sediments is quite low for mining, worth only eleven cents per ton. However, improved mining techniques and concentration methods may make the Gastineau Channel sediments valuable some day. Certainly three samples are not sufficient to evaluate the potential. The analyses of more grab samples and deep cores are required to give a proper assessment of this area.

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CHAPTER V

GOLD ADSORPTION ON CLAYS IN SEA WATER

INTRODUCTION

The association of gold with particulate matter in the oceans has been suggested by Haber (1927), Hummel (1957) and others. Haber (1927) found that he could reduce the amount of gold in solution by centrifuging the samples prior to analysis. Hummel (1957) made his conclusion based on generally higher gold concentrations in near shore waters. The association of gold with particulate matter is an important factor in investigation of the geochemistry of gold in sea water.

The nature of particulate matter varies from one locale to another and with change of season. The amount of clay in the particulate matter may vary from near zero in open ocean water to near 100% in glacial fjords. The scavenging property of ion exchangers such as clay may play an important role in maintaining the apparent undersaturation of this noble metal in sea water. Colloidal gold is known to adsorb on clays even though both carry net negative charges in sea water (Riddick, 1968). Clays have positive charges on the plate edges. Protective colloids such as silica and organics may retard the adsorption process (Krauskopf, 1967). It was decided to investigate the influence of clays upon the gold concentration using a radioactive tracer.

EXPERIMENTAL

The adsorption of gold on particulates was investigated using three standard clays (Wards bentonite No. 20, illite No. 35, kaolinte No. 7) and a natural sediment from southeastern Alaska (clay and fine silt sediment, Gastineau Channel near Douglas). Gulf of Alaska sea water and

distilled water were mixed to obtain solutions of ca. 0, 6, 12, and 18 °/₀₀ chlorinity. Radioactive ^{198}Au in gold carrier as $AuCl_4^-$ was added to each to obtain a concentration of 10 µg Au/l. The pH of all solutions was adjusted to 8.0 ± 0.2 with dilute NaOH. The initial activity was 9, 550 ± 69 (σ) c/min/ml.

Five series of solutions were used, one for each type of particulate matter and one for a control to monitor the adsorption of gold on the 50 ml polyproplyene centrifuge tubes. Approximately 10 mg of each type of particulate matter were mixed with its respective chlorinity series. The mixtures were shaken for 15 min. with a Burrell (wrist action) shaker, then allowed to settle. The solutions were centrifuged for 20 min. prior to removal of 1 ml aliquots for counting. The experiment was followed for one week with the solutions shaken before and after each sampling.

Bentonite was found to behave most like the natural sediment investigated, and was chosen to check the adsorption of gold with varying amounts of particulate matter. Forty milliliters of sea water (Cl = 18 °/₀₀, pH = 8.0) spiked with ^{198}Au were pipetted into five centrifuge tubes. Bentonite in the amounts of 1.4, 10.4, 49.8 and 100.4 mg was added to four of the tubes and all were well shaken. The adsorption was followed for a week in the manner previously described.

RESULTS

The data were corrected for the decay of the radioactive tracer and for the blank. The results for the natural sediment in solutions of varied chlorinity is shown in Fig. 5-1. The concentration of gold in

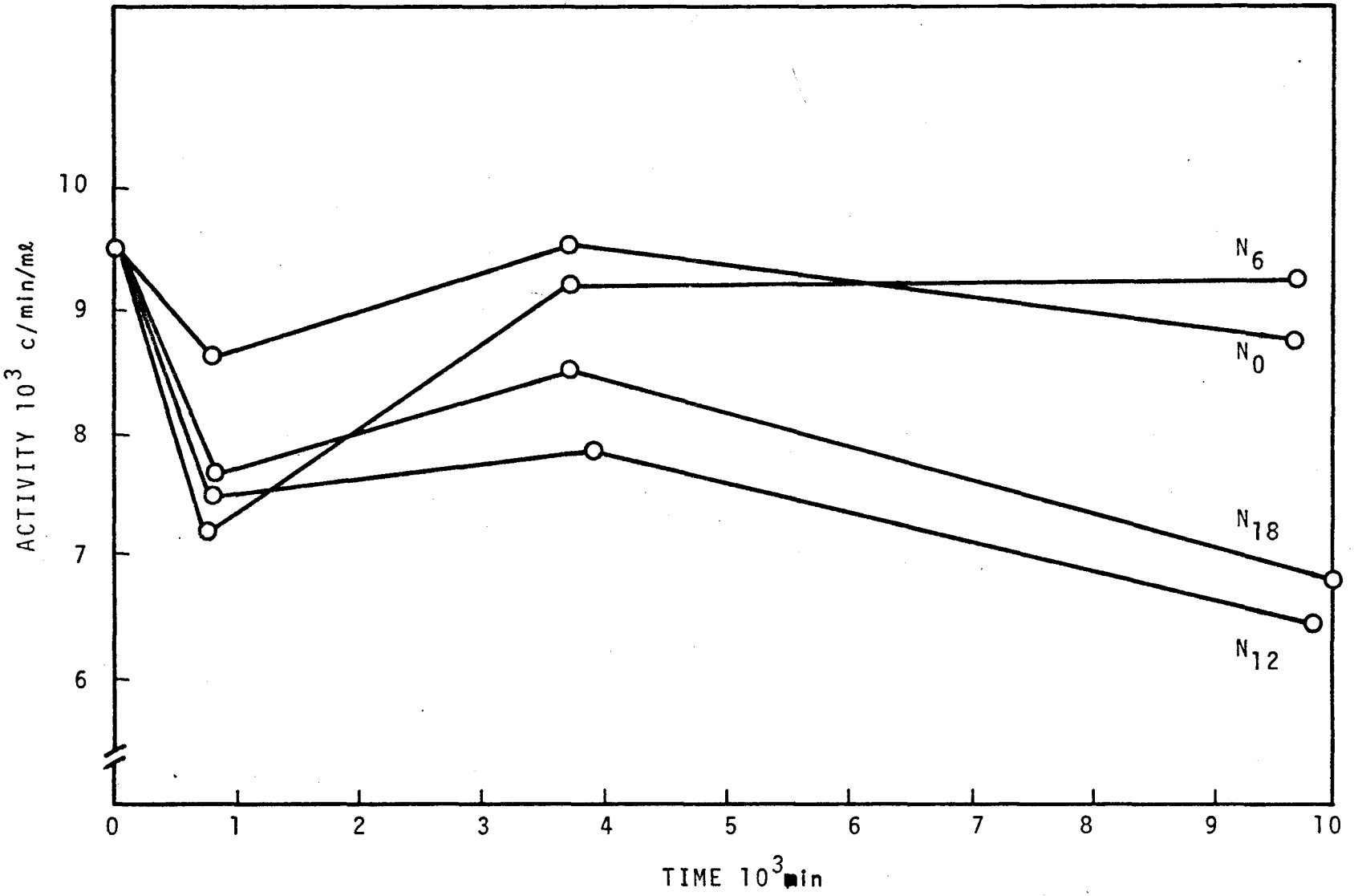

Fig. 5-1 Adsorption of gold on natural sediment at chlorinities 0, 6, 12 and 18 °/₀₀.

solution diminished rapidly in the first 12 hr, followed by a return of gold to solution, and finally a steady, slower loss of gold from solution. Three processes seem to be taking place simultaneously: 1) a rapid adsorption of gold III to clay, 2) the reduction of gold III to gold I with release from the clay, and 3) the slow adsorption of colloidal gold to the clay. The pattern of adsorption based on the chlorinity of the water is as follows: Cl = 6 °/₀₀ $\leq$ Cl = 0 °/₀₀ << Cl = 18 °/₀₀ $\leq$ Cl = 12 °/₀₀. This effect is probably a result of the zeta potential, the charge on the particulate matter which changes with chlorinity, which is usually negative for chlorinity 0 - 6 and increases positively with chlorinity greater than 7 (E. K. Duursma, personal communication).

The behavior of those clay type materials as compared to natural sediments at Cl = 18 °/₀₀ is presented in Fig. 5-2. It is interesting that the intercept based on the slope of the latter part of the curve is coincidental with the initial concentration.

The adsorption of gold from a solution containing 10 µg/l on varying amounts of clay is shown plotted in Fig. 5-3. The same initial adsorption and release of gold as before was seen, and was dependent on the amount of clay present with no definite trend shown after two to three days.

CONCLUSIONS

Gold III chlorohydroxy complexes are adsorbed on clay in direct proportion to the amount of clay present. The adsorption is also a function of chlorinity with the most dramatic increase seen between Cl = 6 °/₀₀ and Cl = 12 °/₀₀. The time span for the initial adsorption and

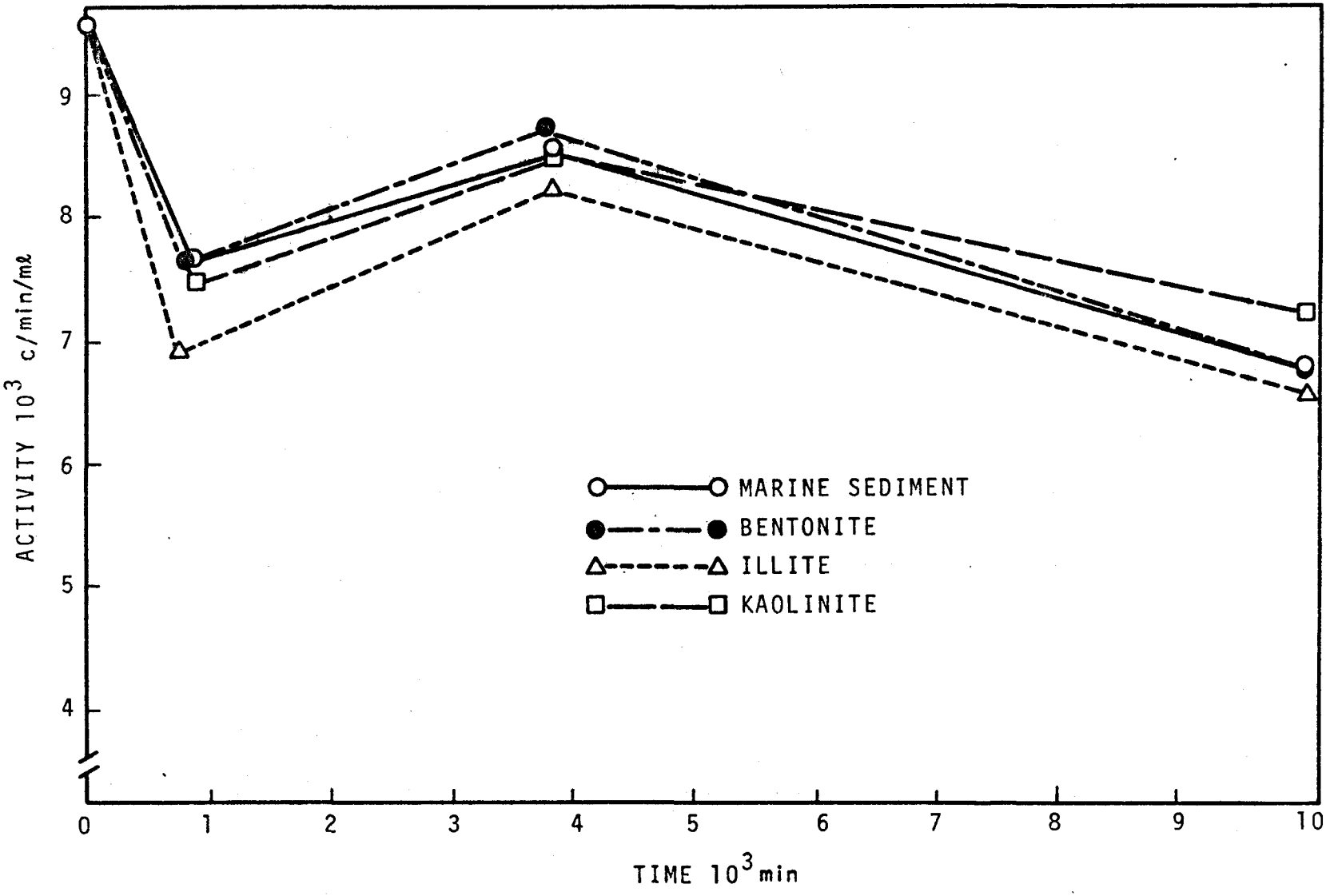

Fig. 5-2 Adsorption of gold on clays (natural, bentonite, illite and kaolinite) at a chlorinity of 18 °/₀₀.

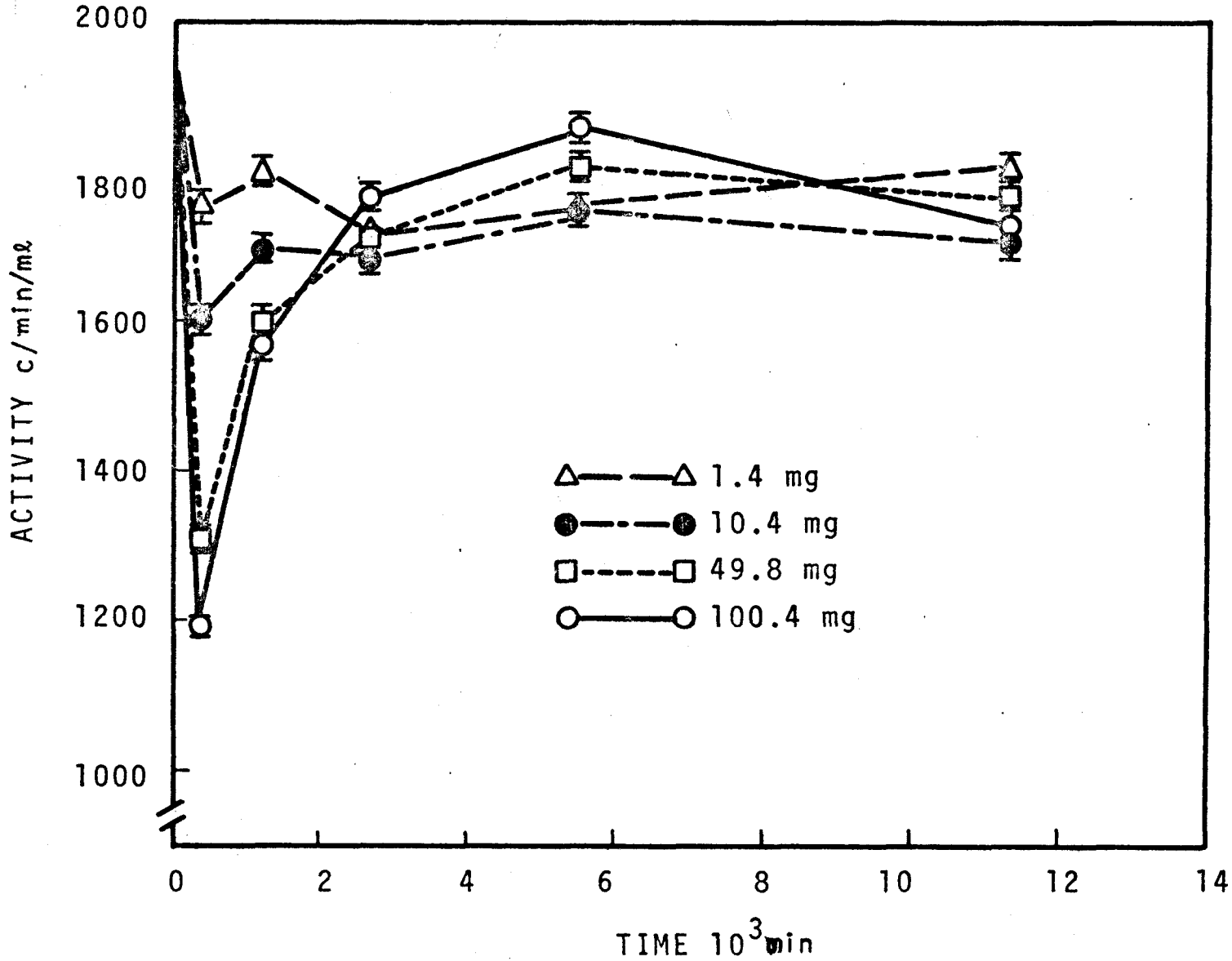

Fig. 5-3 Adsorption of gold on various amounts of bentonite at a chlorinity of 18 °/₀₀.

release of gold is on the same order as for equilibrium in the reaction

$$AuCl_4^- + 2Au + 2Cl^- \rightleftharpoons 3AuCl_2^- \qquad K_{eq} = 1.8 \times 10^{-8} \qquad (5\text{-}1)$$

(Lingane, 1962). Particulate matter, especially ion exchangers such as clays, probably provide sites for reduction of gold from Au^{3+} to Au^{+1}. Since gold is a good oxidizing agent,

$$AuCl_4^- + 3e^- \rightleftharpoons Au + 4Cl^- \qquad E^o = 1.00v \qquad (5\text{-}2)$$

most reduced metals could substitute for the metallic gold on the left side of equation 5-1 (Krauskopf, 1967). After two to three days the loss of soluble gold was independent of the amount of clay present. Gold I chlorohydroxy complexes seem not to adsorb on clays, but to be affected primarily by the solution chemistry (equation 5-1). The clays then appear to adsorb colloidal gold once it is formed. Colloidal gold is formed by the shift of equation 5-1 to the left and by the reaction of aurous chloride with water, especially in a slightly basic solution such as sea water:

$$AuCl_2^- + OH^- \rightleftharpoons AuOH + 2Cl^- \text{ (Remy, 1956)} \qquad (5\text{-}3).$$

The total adsorption in this study was relatively small, approximately 10%. However, the effect may be quite dramatic in glacial fjords, where gold-bearing sea water is mixed with glacial drainage containing large amounts of clay.

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CHAPTER VI

DISTRIBUTION AND FORMS OF GOLD IN OPEN OCEAN AND COASTAL WATERS

INTRODUCTION

It is generally accepted that the concentration of gold in sea water is far too low to be economically extracted by any means presently available, even in select areas where high gold anomalies may exist. However, knowledge of the geochemistry of gold in the marine environment may point to a natural concentration process by which gold may be extracted either for itself or as a byproduct.

Two areas in southeastern Alaska near known land gold deposits were chosen for study. Reid Inlet, in Glacier Bay National Monument, drains a highly glaciated area which contains some low-grade gold ore. The suspended particulate matter in the Inlet is almost entirely glacial detritus. The second area, Gastineau Channel, receives the drainage from the famous Juneau gold fields. The water contains a significant amount of organic matter. Both water and sediment samples were taken from streams draining these gold bearing areas, as well as from the water column in the adjacent estuaries and underlying unconsolidated sediment (Fig. 6-1). The water was filtered, acidified and passed through columns of strong anion exchange resin. Portions of the original samples were acidified for subsequent determination of total gold content.

Lake Nitinat, an anoxic fjord located on Vancouver Island, was investigated as a special case because of the high sulfide content. Water was obtained from several open ocean areas for comparison with coastal areas. Two cruises were made into the Gulf of Alaska and northeast Pacific Ocean. Water was also obtained from the east Pacific and Caribbean Sea.

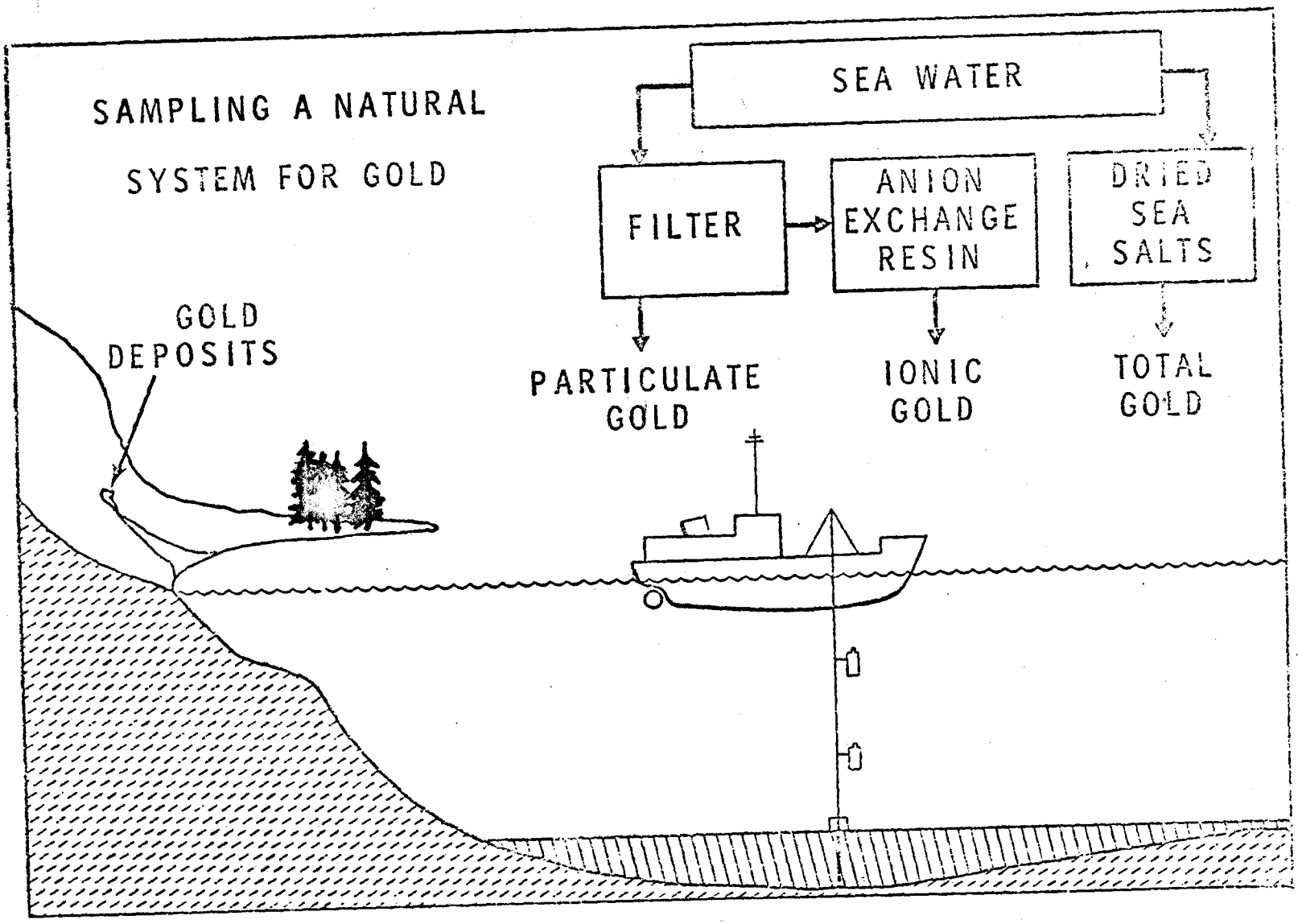

Fig. 6-1 Schematic for sampling the natural system and handling the samples.

DESCRIPTION OF AREAS SAMPLED

Reid Inlet, Glacier Bay

Reid Inlet is located in the northwestern part of Glacier Bay in the Glacier Bay National Monument of southeastern Alaska (Fig. 6-2). The area has recently been heavily glaciated and is for the most part devoid of vegetation. The inlet (Fig. 6-3A) is bordered on the east and west by steep cliffs covered with glacial debris. Reid Inlet faces north just south of Russell Island, and is fed by the retreating Reid Glacier. Reid Inlet measures approximately 0.9 by 3.5 km. The relatively flat bottom slopes gently toward the entrance from 45 m, 0.8 km north of the glacier face, to 50 m just inside the 12 m terminal moraine sill (Fig. 6-3B). The depth increases sharply to 375 m in Glacier Bay. The Inlet is usually dotted with numerous chunks of ice, most of which melt (in summer months) before leaving the inlet, creating a surface layer of low-salinity water containing large quantities of fine glacial detritus. Suspended organic matter results from plankton in the "new" sea water which enters between ca 10 - 16 m. The lower water is probably flushed seasonally.

The country rock of the area is dominated by granodiorite, which intrudes metamorphosed sedimentary rocks (conglomerate, limestone, and black graphitic schist) probably of Paleozoic Age (Rossman, 1959). The area, especially west of Reid Inlet, contains numerous lenticular quartz veins, which have altered the country rock to 3 m on either side of the veins. The location of gold mineralization both in the altered rock and veins is spotty and unpredictable. Several of the veins have been mined.

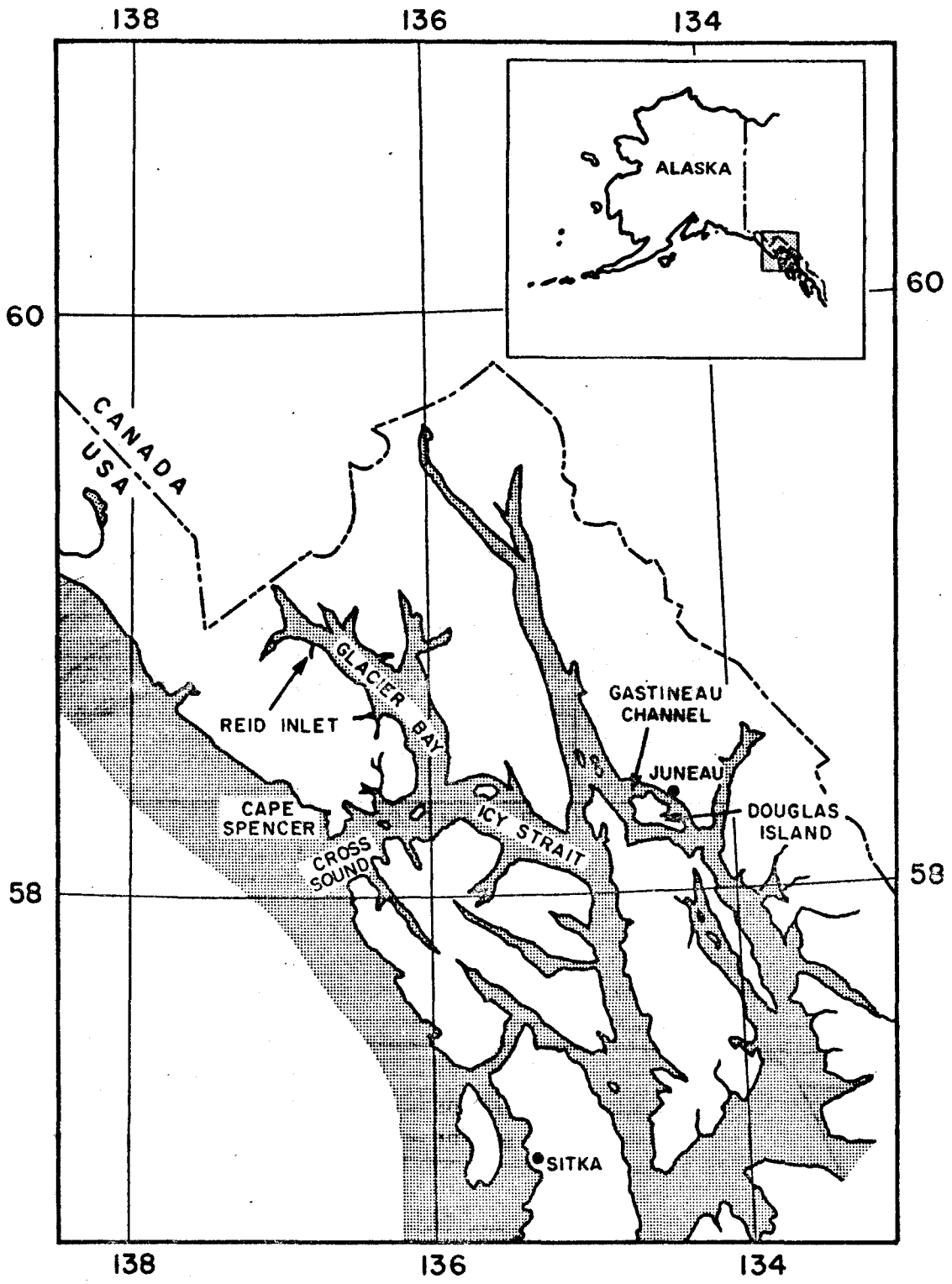

Fig. 6-2 Map of southeastern Alaska showing general location of Gastineau Channel and Reid Inlet.

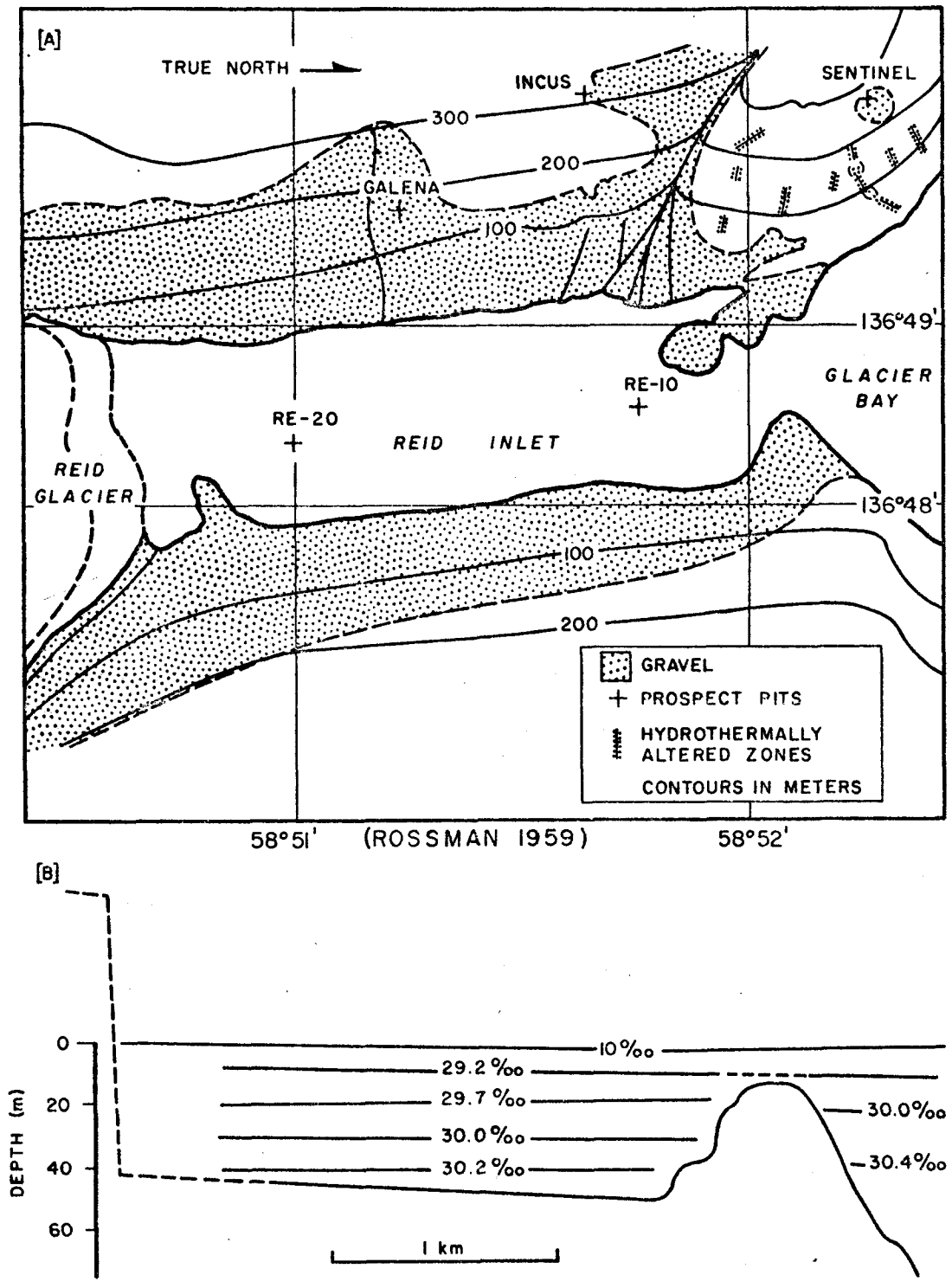

Fig. 6-3 Reid Inlet, Glacier Bay, Alaska showing (a) the contours and locations of some gold deposits and (b) the cross-section with the shallow sill and salinity distribution.

The granodiorite is believed to be part of the Coast Ranges batholith of Cretaceous age. Since batholithic intrusion, the area has been cut by numerous vertical mafic dikes running east and west.

The gold-bearing fluids entered along pre-existing fractures in the sedimentary and granodiorite rocks. In some cases, the emplacement was inhibited by the dikes. Some gold has been taken from rock containing galena along the west shore of Reid Inlet near the entrance. The gravels along the northwest shore of Reid Inlet have been worked for placer gold. Gold deposits on the east side of Reid Inlet are low grade.

Gastineau Channel, Juneau

Gastineau Channel separates Douglas Island from the mainland in southeastern Alaska. The Channel runs southeast from Juneau emptying into Stephens Passage (Fig. 6-2). The two highest producing gold mines of the one-hundred-mile-long Juneau gold belt are located near Juneau (Fig. 6-4). Run-off from these and smaller, gold-bearing areas drain into Gastineau Channel.

The Juneau gold belt lies between the Coast Range diorite batholith core to the east and greenstone chloritic schists to the west (U.S. Bureau of Mines, 1967). Wide lodes containing low-grade stringers parallel to the foliation of the schistose or slaty country rock are the most productive (U.S. Senate, 1964). The gold at the Alaska - Juneau mine is in irregular quartz stringers and gash veins which intrude metamorphosed sedimentary rocks. At the Alaska Treadwell mine the gold is evenly distributed in mineralized albitediorite dikes which intrude black slate.

Much of the area which drains into Gastineau Channel is well

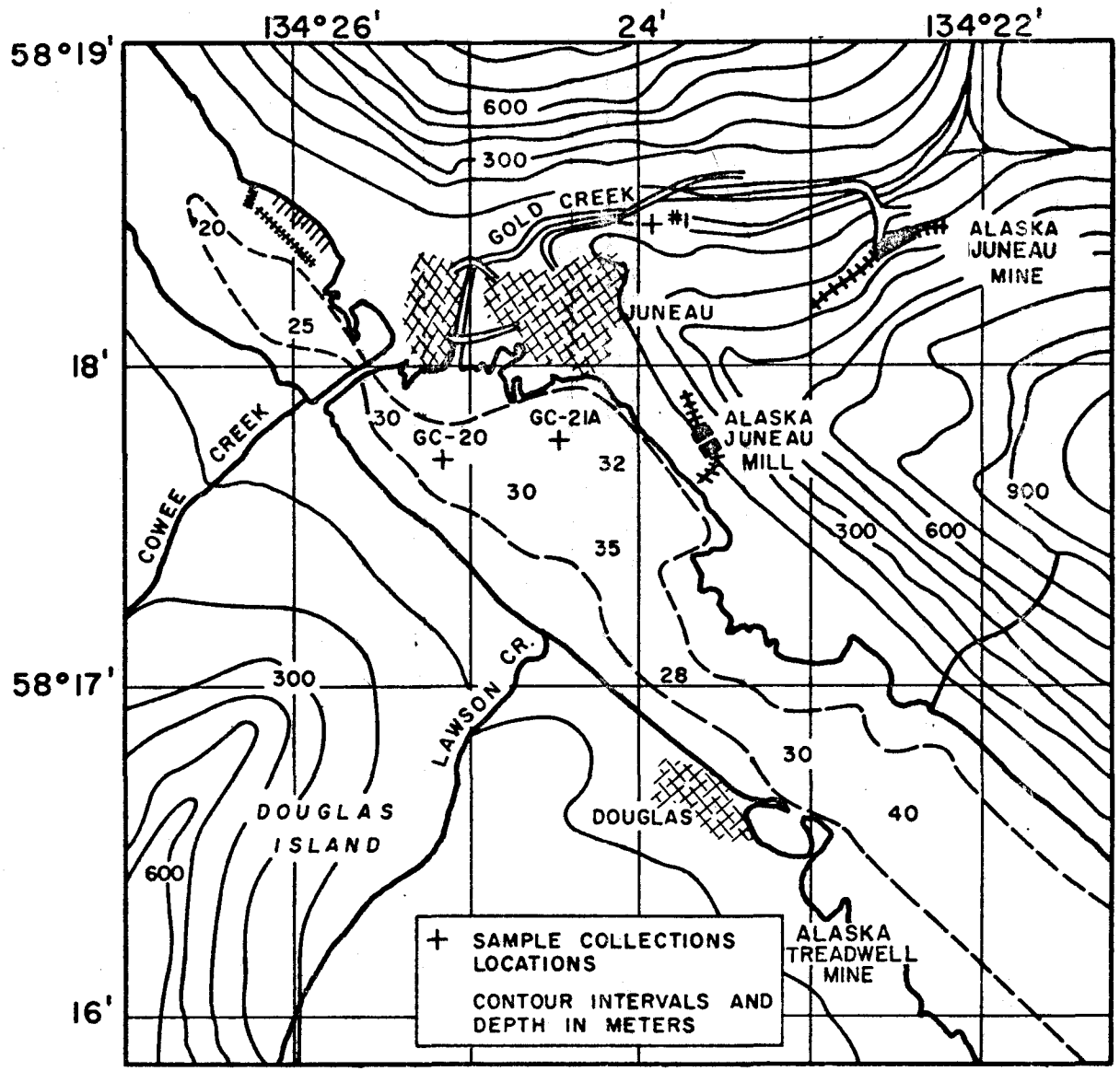

Fig. 6-4 Location of Gastineau Channel stations and Gold Creek where samples were obtained. Major gold mines in the Juneau-Douglas area are also shown.

vegetated with trees (spruce and alder) and low brush. The Channel receives considerable organic material from the towns of Juneau and Douglas and from the moderately high local primary productivity.

Lake Nitinat, Vancouver Island

Lake Nitinat (pronounced Nit-nat) is an anoxic fjord located on southwestern Vancouver Island, British Columbia. The fjord is about 23 km long by 1.2 km, with a maximum depth of about 200 m. The fjord receives variable amounts of sea water from the Pacific Ocean over a narrow 4 m sill entrance at the southerly end. The influx of fresh water from numerous streams produces a highly stratified system. The lower waters are always devoid of oxygen and high in organic degradation products, including hydrogen sulfide. The chemical system is well described by Richards et al. (1965).

Open Ocean

The northeast Pacific, including the Gulf of Alaska, is characterized by a counter-clockwise gyre produced by the northerly-flowing branch of the Kuroshio Current (Sverdrup et al., 1942). The usually turbulent surface waters are well mixed to depths greater than 100 m. An oxygen minimum layer exists from about 250 to 750 m depth. Surface waters flow north through the Aleutian Islands into the Bering Sea from the westerly-flowing North Pacific surface water (Fig. 6-5). Most open ocean waters contain little particulate matter because of low productivity and the lack of land derived debris. Even the surface waters rarely contain greater than 1 mg/l of particulates.

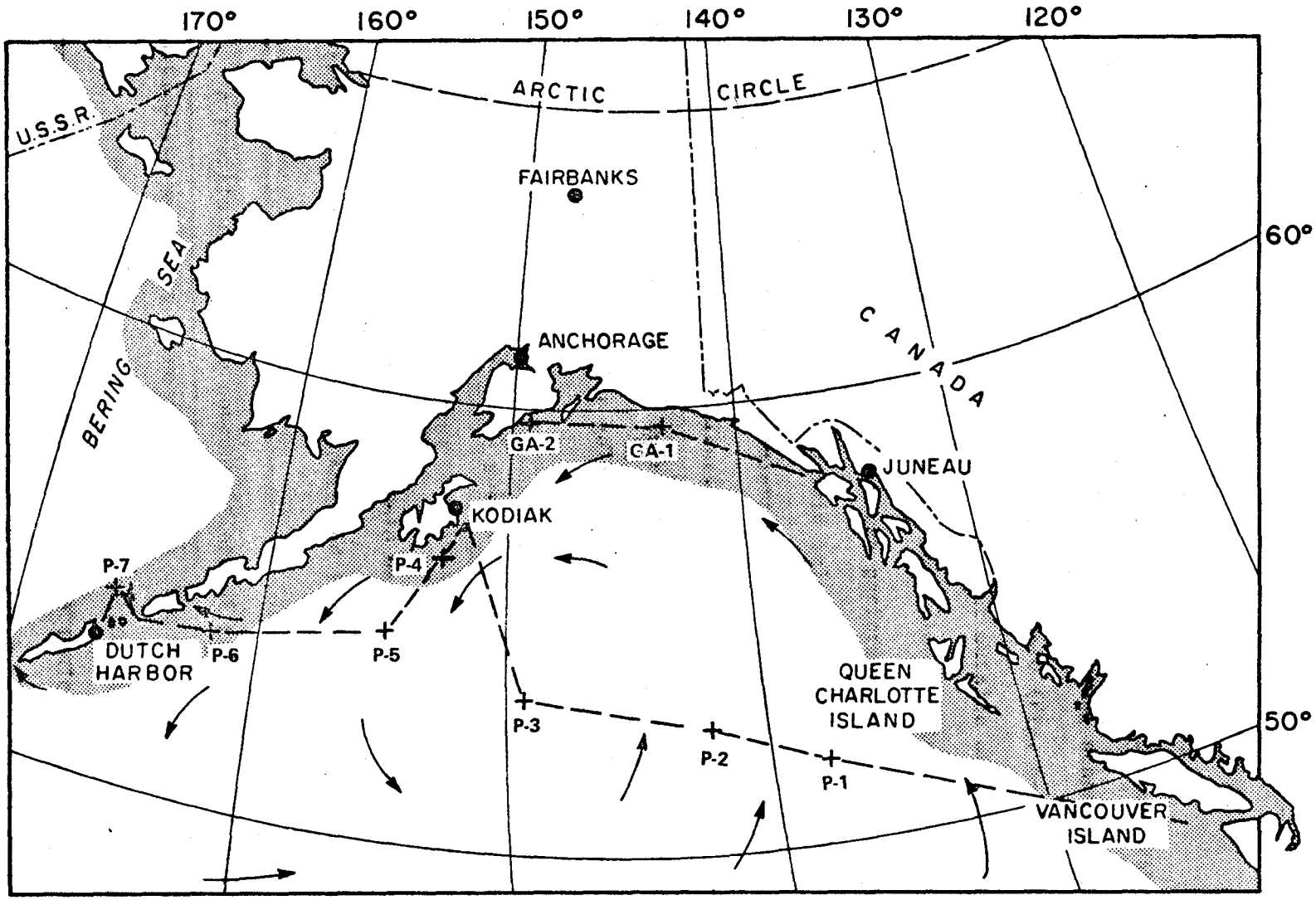

Fig. 6-5 Map of northeast Pacific Ocean and Gulf of Alaska showing surface current direction and cruise track of USC & GS RAINIER. Location of Gulf of Alaska station GA-1 is shown near the coast of south central Alaska.

RESULTS

Reid Inlet, Glacier Bay

Reid Inlet was sampled in September, 1968 (ACONA Cruise 074) and in April, 1969 (ACONA Cruise 089). The general sampling scheme outlined in Fig. 6-1 was followed on stations RE-10 and RE-20 (Fig. 6-3A) on the first cruise. Glacier Bay station GL-40 just outside of Reid Inlet and GL-15 near the entrance to Glacier Bay were also sampled.

An abbreviated sampling program was performed on the second cruise. Only station RE-10 was sampled in Reid Inlet along with a station outside the inlet. The suspended particulate matter was removed from the water by centrifuging rather than filtering as was done on the first sampling. The salts were dried under an infrared lamp as opposed to freeze drying. The samples were analyzed for gold by neutron activation by methods described in Chapter II.

The concentrations of total gold in the water column are shown in Fig. 6-6. Generally high values were noted at Reid Glacier, RE-20, and near the entrance to Glacier Bay. Gold values in the relatively calm waters of RE-10 and GL-40 were lower and fairly consistent at about 3 ng Au/l.

A profile showing the concentrations of gold associated with particulate matter is shown in Fig. 6-7. The values are generally low, about 10% of the total gold. The concentration of ionic gold is also about 10% of the total (Fig. 6-8). Both the ionic and particulate fractions of gold generally decrease with depth. The total gold concentration in the clear water stream on the west side of Reid Inlet (near

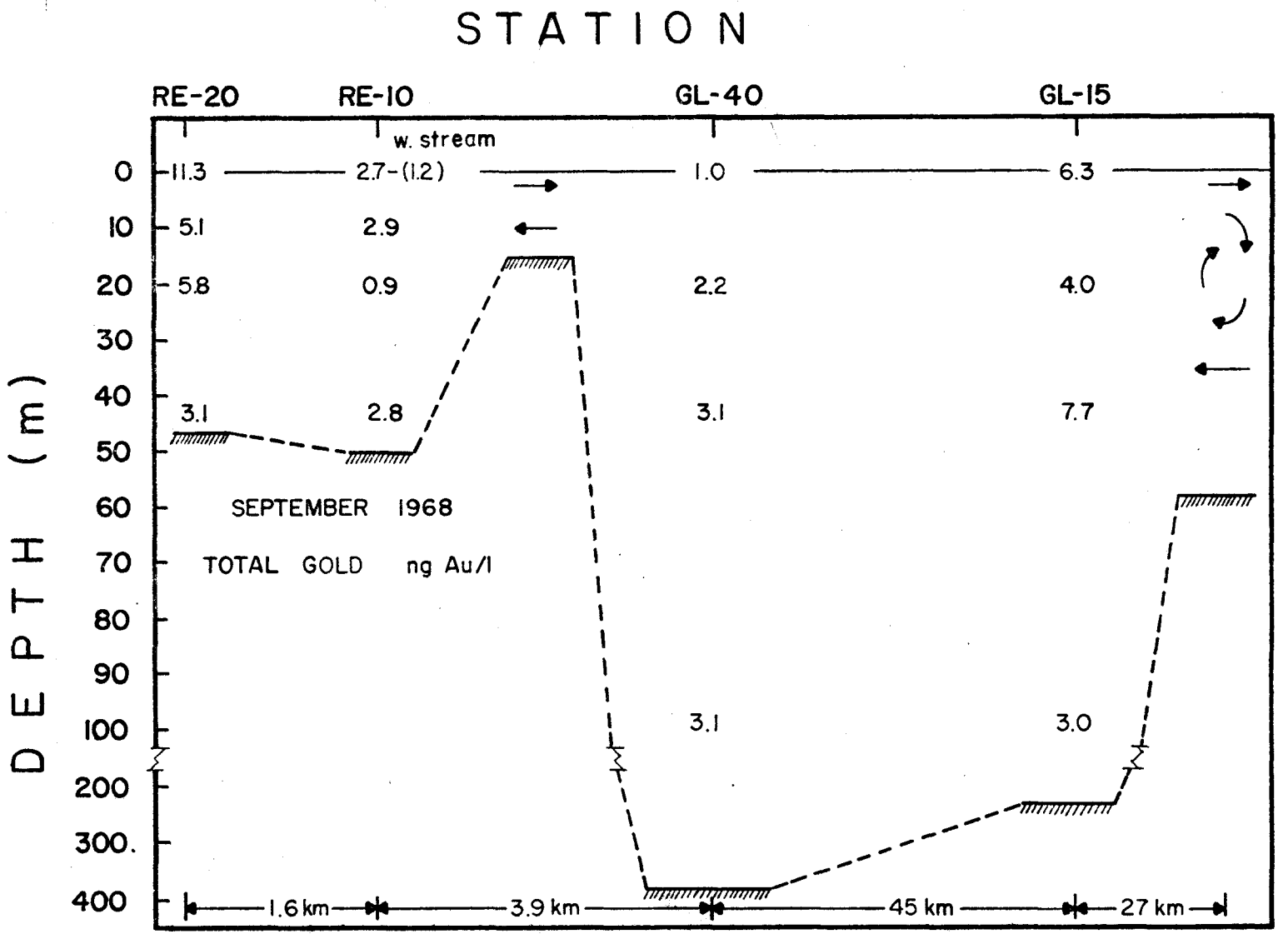

Fig. 6-6 Distribution of total gold in Reid Inlet and Glacier Bay.

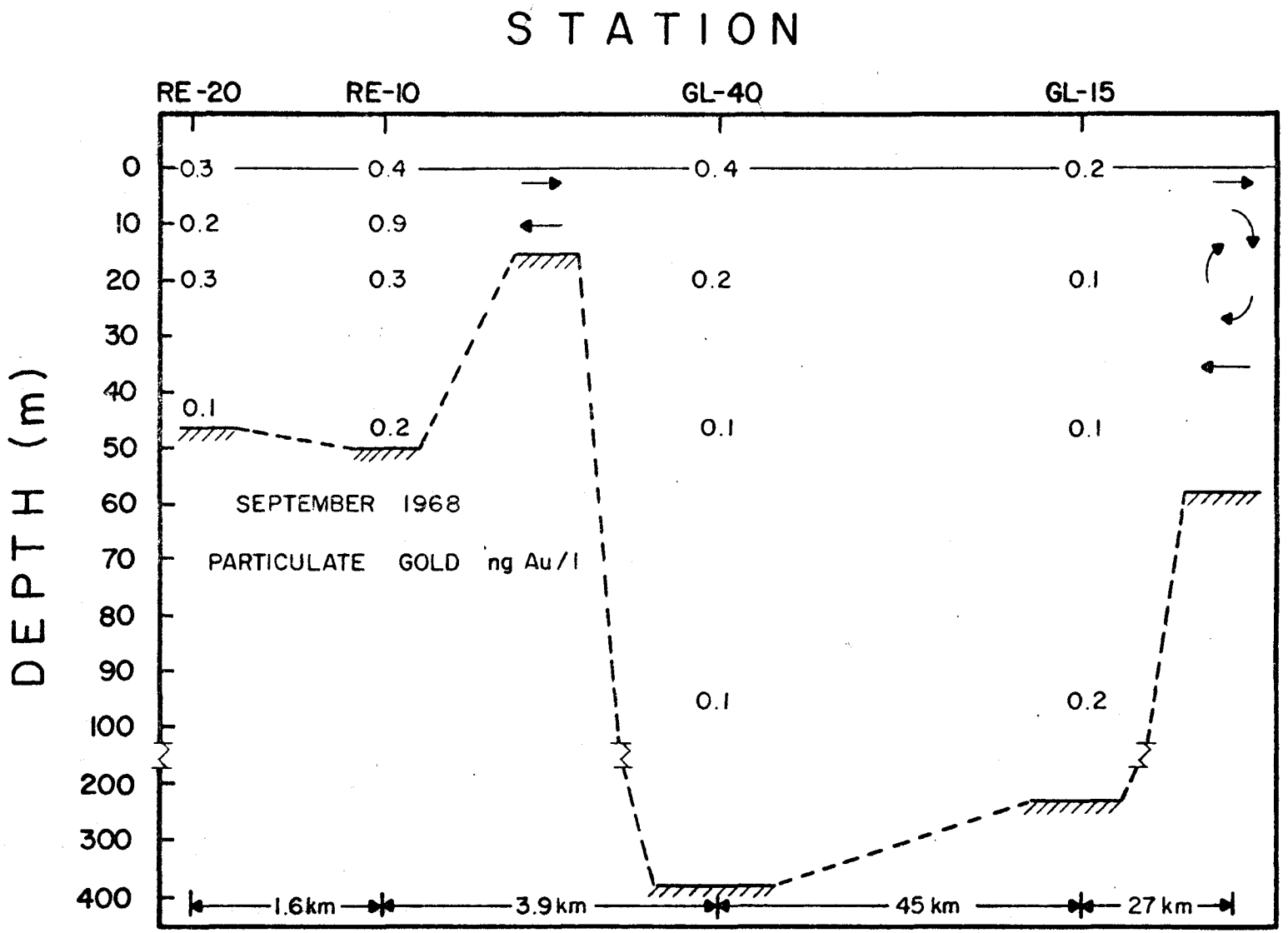

Fig. 6-7 Distribution of gold associated with particulate matter in Reid Inlet and Glacier Bay.

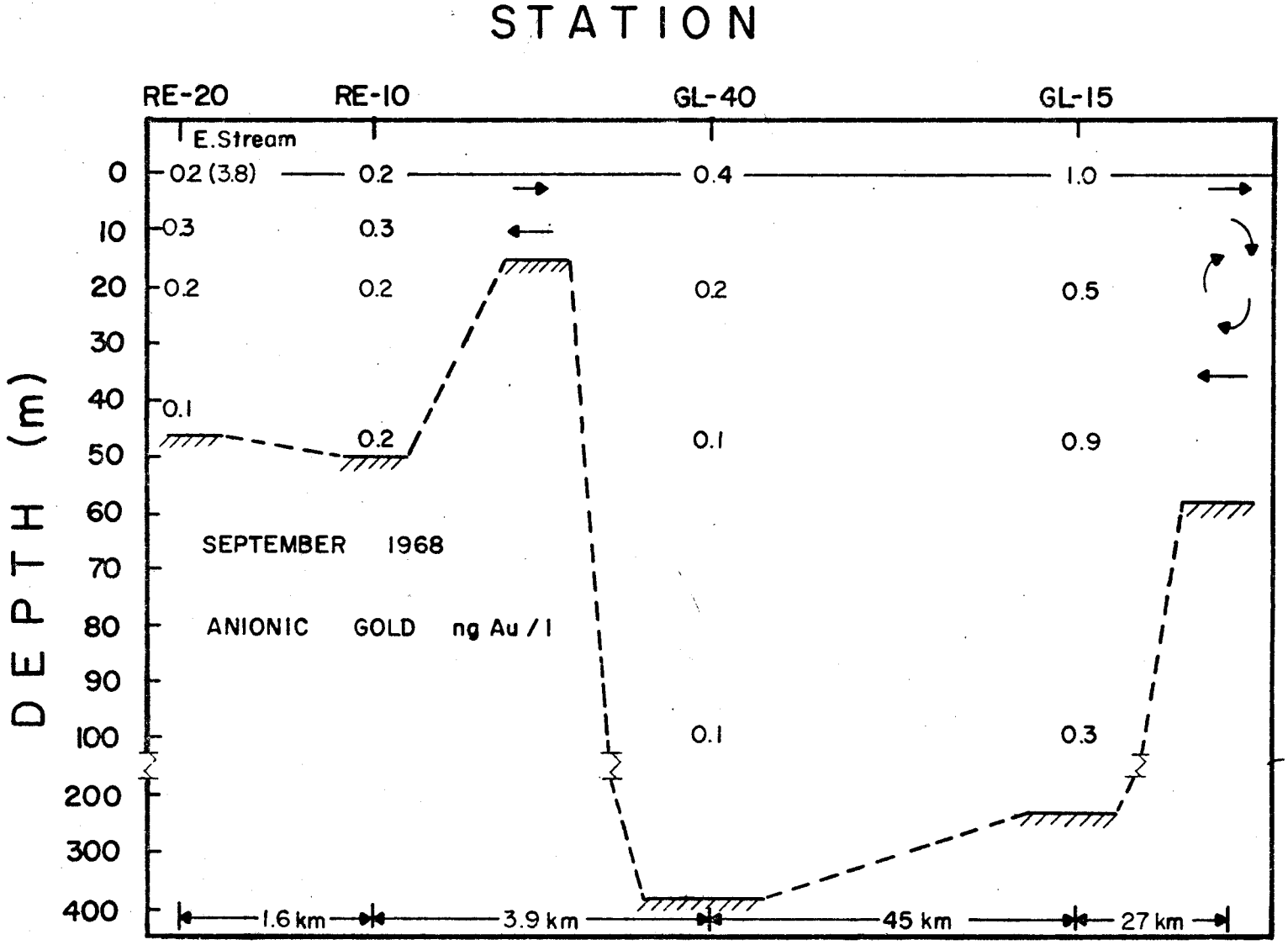

Fig. 6-8 Distribution of anionic gold in Reid Inlet and Glacier Bay.

RE-10) was 1.2 ng Au/l. This amount only served to decrease the concentration of gold in the surface waters. The dilution of the surface water by run-off and ice melt is demonstrated by the low σ_t value for RE-10 (Fig. 6-9).

A total gold concentration was not obtained from the stream which emptied into the east side of Reid Inlet between the glacier and station RE-20; however, a relatively high ionic gold concentration of 3.8 ng Au/l was found. This may account for the high gold values found in the surface water of station RE-20. The suspended sediment load for this stream was more than 17 g/l.

Evidence of flushing of the inlet water during the 1968-69 winter is shown in Fig. 6-10. The profile of RE-10 shows an increase in water density (σ_t), dissolved oxygen (O_2) and pH. The increase of σ_t was due both to a decrease in temperature and an influx of high salinity water. The difference in the concentration of dissolved oxygen in the deep water is probably a good indication of the degradation of biological material occuring during the spring and summer months.

The gold concentrations are fairly consistent at 2-3 ng Au/l with some depletion at mid-depths. The particulate and ionic gold (Fig. 6-11) follow the trend of the total gold concentrations with highest values at the pycnocline (10 m).

Sediment from station RE-10 was obtained in a grab sample and a core. The core material was light grey in color except for thin black layers characteristic of cores from these glacial inlets. The black layers were about a centimeter thick and spaced 20 to 40 cm apart. These layers probably represent organic matter deposited during the winter when

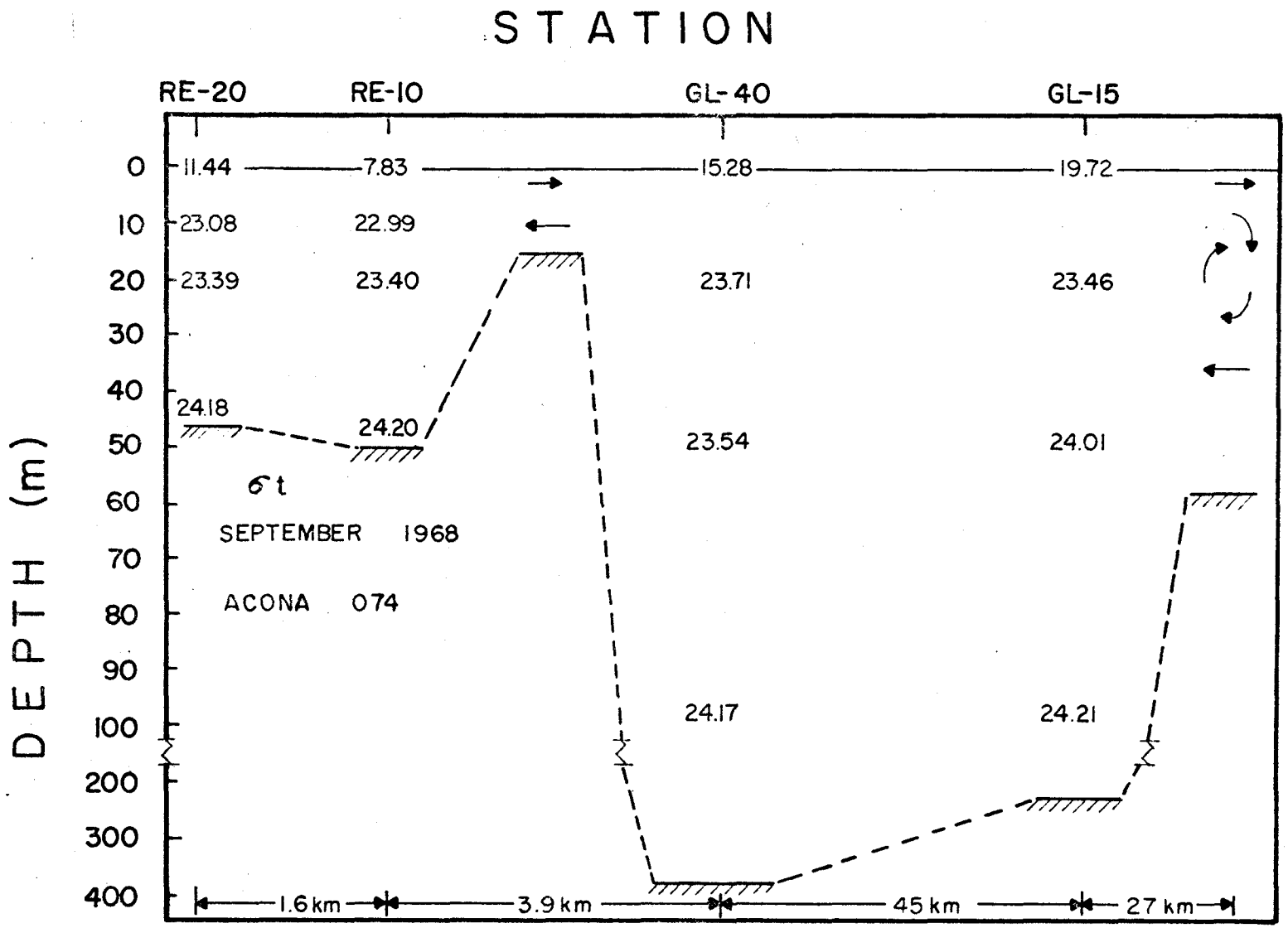

Fig. 6-9 Density (σ_t) distribution in Reid Inlet and Glacier Bay.

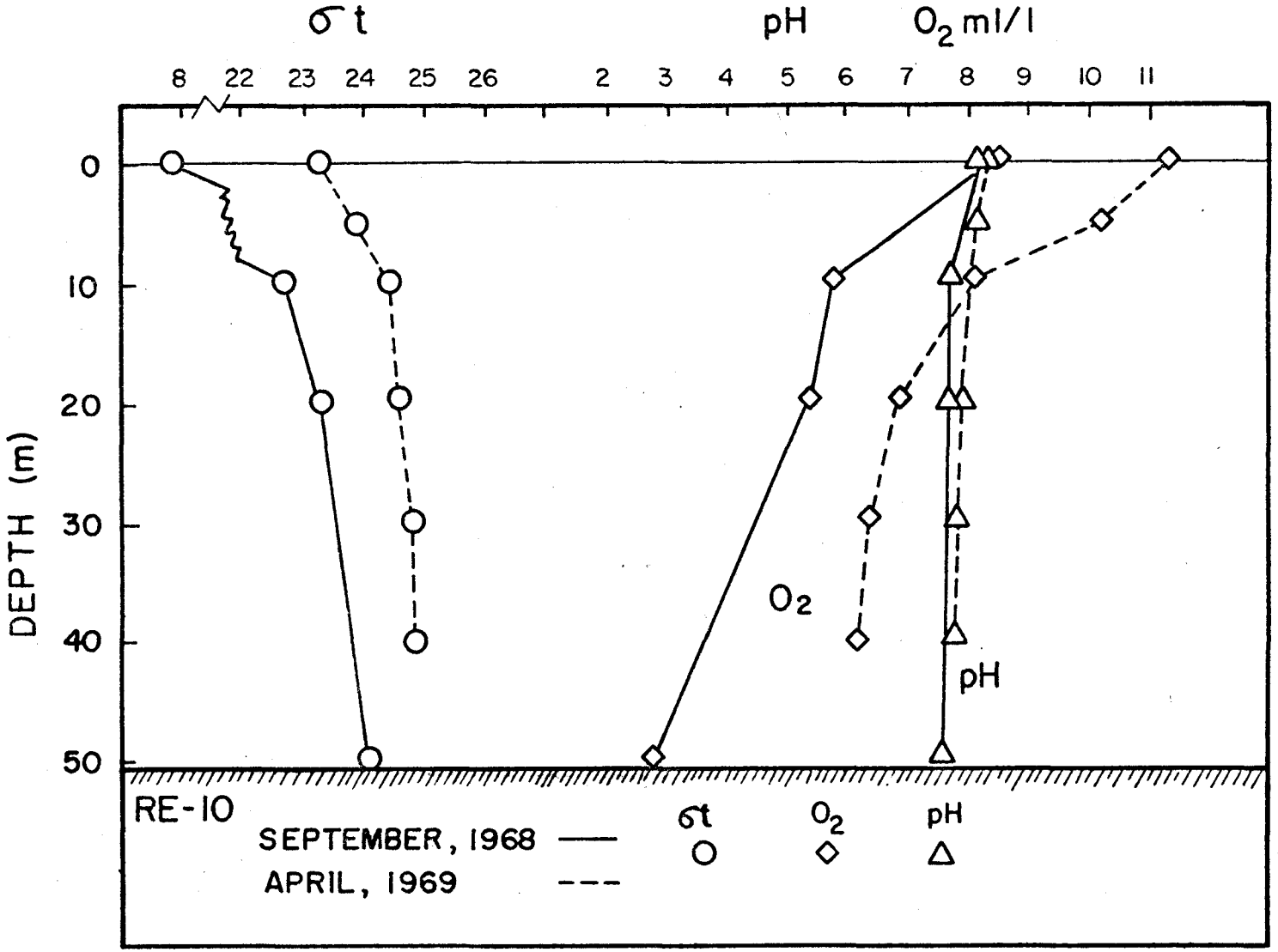

Fig. 6-10 Differences in O_2 and pH in profile for Reid Inlet (RE-10) between September, 1968 sampling and April, 1969.

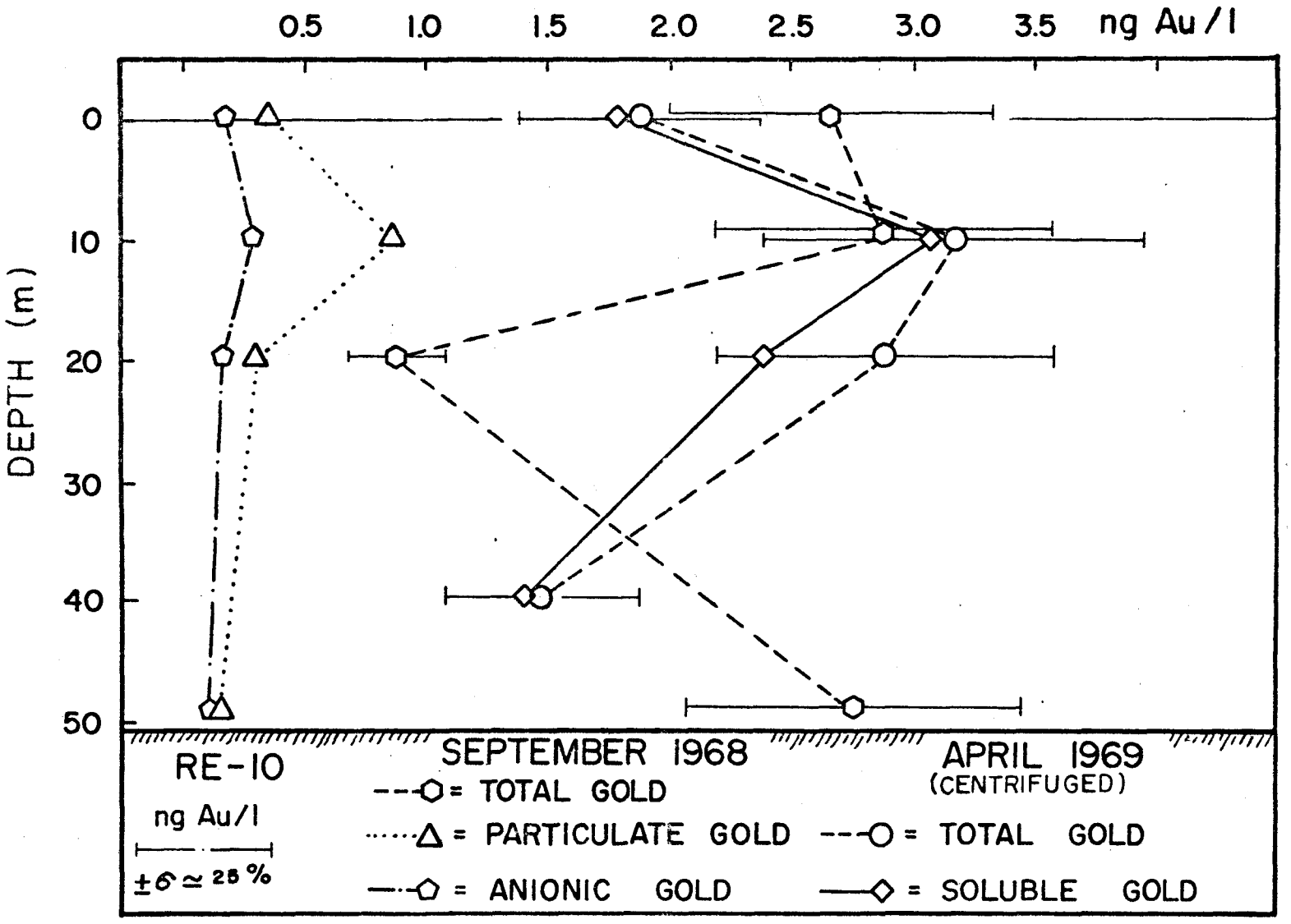

Fig. 6-11 Vertical distribution of gold (anionic, particulate and total) in Reid Inlet (RE-10), September 1968 and April 1969.

the flow of glacial detritus into the inlet was minimal. If these are annual occurrences, they provide a good record of annual sedimentation rates. Just below one black layer was a 4 cm layer of light tan silt-sized sediment followed by a sandy layer 2 cm thick. The remainder of the core material was a mixture of sand and silt as was the material collected in the grab.

Analysis of the various layers gave values of:

	µg Au/g Sediment	Layer Thickness (cm)
Grab sample	0.013 ± 0.002	-
Core, Black Layer	0.039 ± 0.007	1
Silt Layer	0.006 ± 0.001	4
Sand Layer	0.025 ± 0.005	2

The grab sample was well mixed and is probably representive of the sediment in this area. The higher gold value in the black layer possibly represents gold associated with biological material brought in by new sea water from Glacier Bay during the winter months. The light tan colored silt deposited just prior to the black layer could have been a result of low run-off and settling of suspended particles in the Fall. The sand layer may be the result of a high velocity flow strong enough to keep the fine sediments in suspension and to transport the heavier particles of gold.

Gastineau Channel, Juneau

Stations GC-20 and GC-21A were occupied in April, 1969 (ACONA Cruise 089). Water was also collected from Gold Creek near the spot marked #1 in Fig. 6-4 and at the mouth of Gold Creek. The concentration of gold

associated with particulate matter was determined both from filtered samples and by centrifuging portions of water. The centrifuged water was analyzed for "soluble" gold. The sum of the centrifuged particulate gold and "soluble" gold is presented as "total" gold in Fig. 6-12. The correlation between the two methods for determining particulate gold is erratic; however, the average in both cases is 0.2 ng Au/l, <10% of the total gold. Centrifugation of samples is desirable as a step to reduce contamination. The total gold concentration is fairly consistent at 3.0-3.5 ng Au/l. The uniformity of the lower water (i.e., below 10 meters) is shown by the plots of σ_t, O_2 and pH shown in Fig. 6-13 and indicates that the "soluble" gold concentration at the 20 m depth was in error. The concentration of soluble gold in Gold Creek above and below Juneau was 0.06 and 0.6 ng Au/l respectively. The higher value near the mouth of Gold Creek probably reflects the increase in chloride which is important in forming gold complexes.

Lake Nitinat, Vancouver Island

One sample of deep water and a sediment sample were obtained for gold analysis from station 2 in Lake Nitinat in July 1968 by W. W. Broenkow, University of Washington. The concentration of H_2S in the sample was not measured; however, it could be expected to be on the order of 300 ug-at. $S^{=}$/l (Richards et al., 1965). The suspended particulate matter was 1.2 mg/l and the results of the gold analysis (ng Au/l) were:

Water		% of Total
Total	5.6 ± 1.4	
Particulate	1.2 ± 0.2 (2)	21

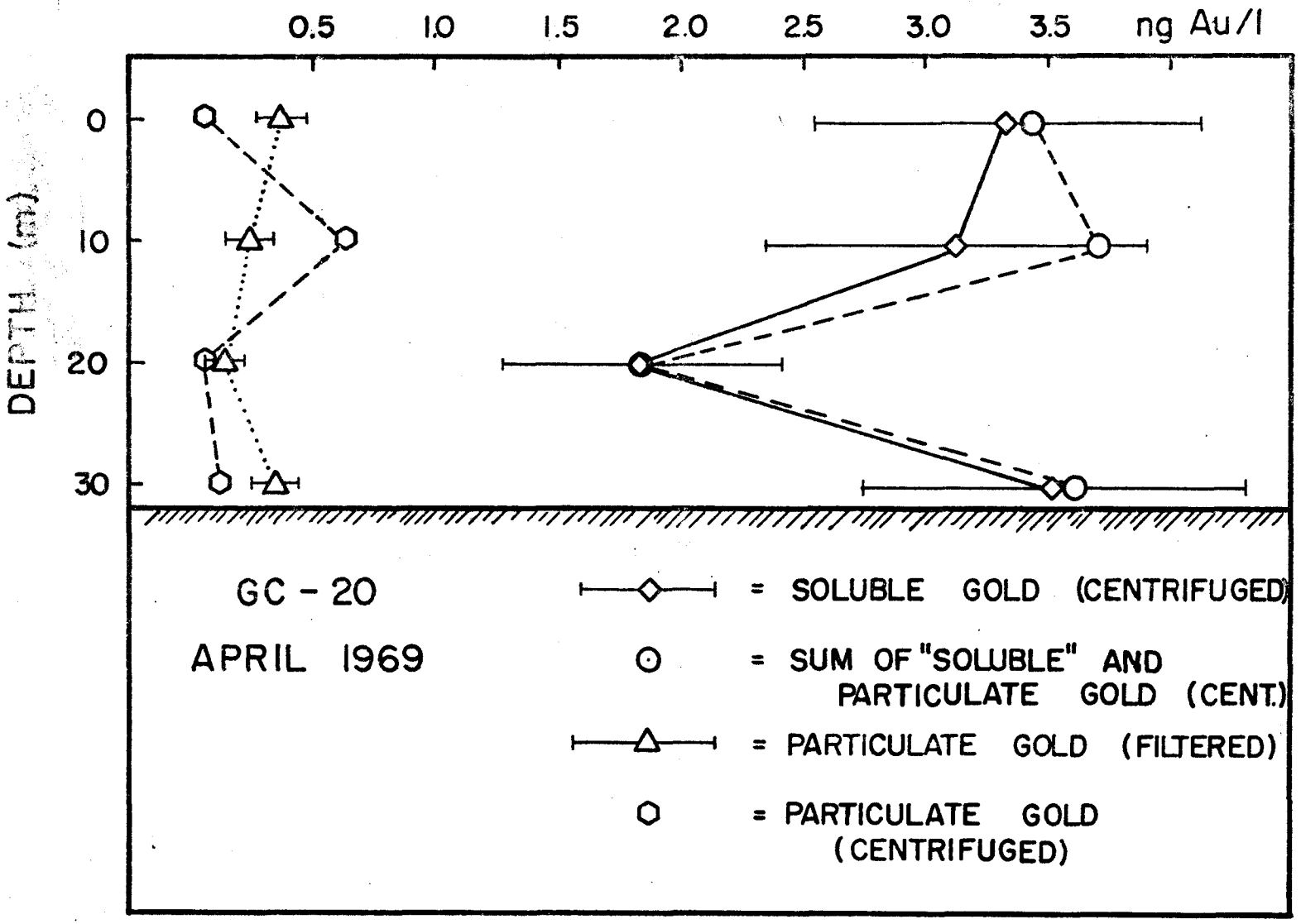

Fig. 6-12 Vertical distribution of gold in Gastineau Channel (GC-20).

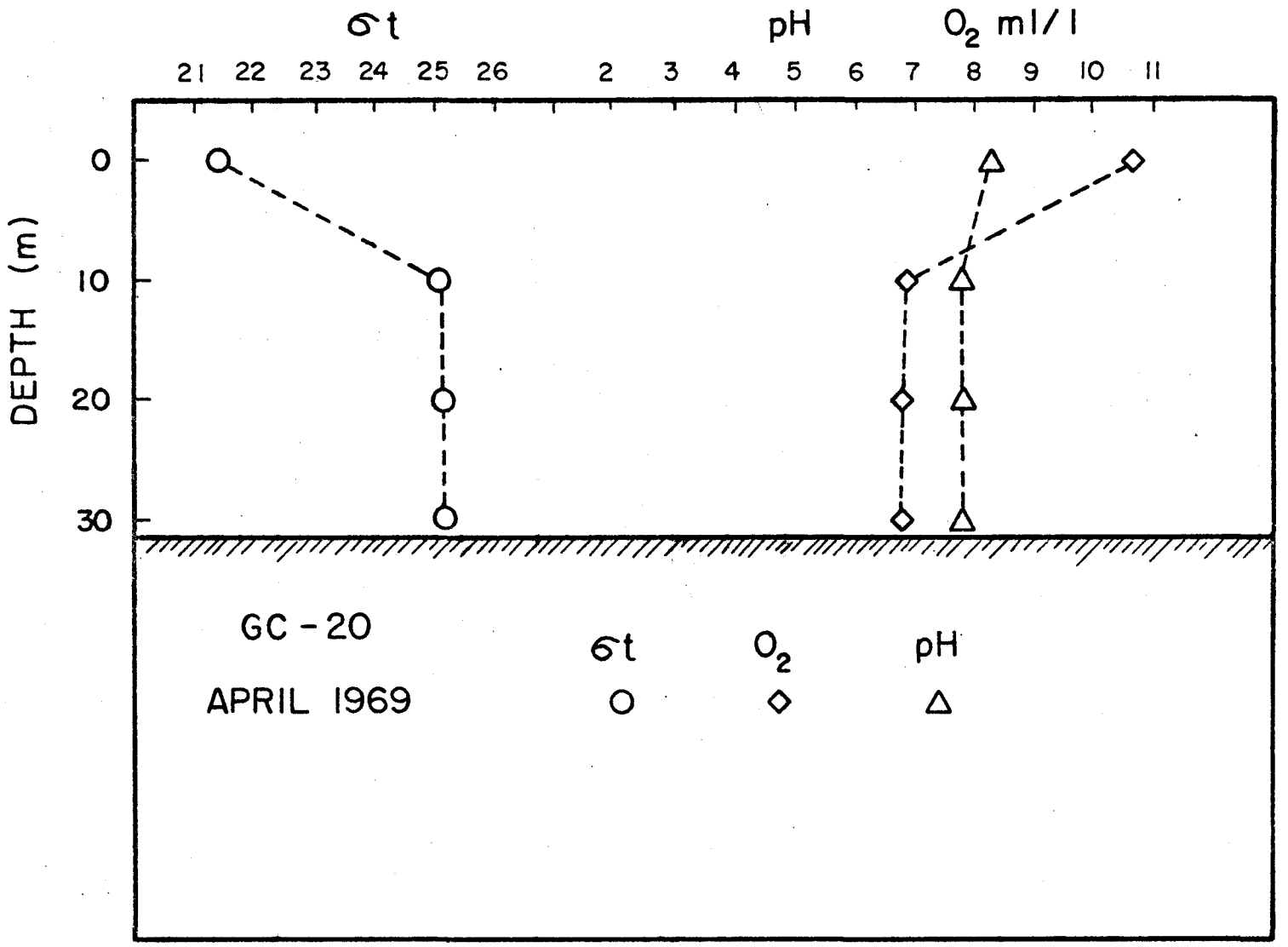

Fig. 6-13 Vertical distribution of σ_t, O_2 and pH in Gastineau Channel GC-20.

Ionic	0.6 ± 0.2 (6)	11
Sediment	0.022 ± 0.009 ug Au/g sed.	

The total gold content of the saline deep water (S = 31.2 °/₀₀) is of the same magnitude expected for non-sulfide bearing waters indicating that gold is not precipitated by H_2S under these conditions. Also the sediment is not particularly rich in gold. The water sample was acidified when drawn and the separations performed several weeks later. The concentrations of particulate and ionic gold in the sample and their ratio is very similar to those found in acidified Gastineau Channel water. The fact that a significant amount of soluble gold was found in the sulfide waters confirms the tracer work described in Chapter III. Gold entering the system as a chlorohydroxy complex probably undergoes a rapid change to the sulfide complex:

$$AuClOH^- + HS^- \rightleftharpoons AuS^- + Cl^- + H_2O \qquad (6\text{-}1).$$

If the soluble non-ionic gold is a colloid, it may be unaffected by the presence of hydrogen sulfide.

Open Ocean

A hydrographic station in the Gulf of Alaska (GA-1) was occupied on ACONA Cruise 064 in May 1968. The water column was sampled to a depth of 1000 m. The PVC Van Dorn type sampling bottles used on this cruise were not equipped with reversing thermometers. Temperature measurements were made using Nansen bottles. Salinity and pH were determined in water from both types of sampling bottles. Only particulate and ionic gold concentrations were obtained at this station (the raw data are in the Appendix). The Nansen and Van Dorn bottles were spaced 5 to 25 m apart.

While the surface waters were well oxygenated, the dissolved oxygen decreased rapidly below the pycnocline (100 m) to near zero at 500 m. This decrease was accompanied by a decrease in pH (Fig. 6-14). The concentration of ionic gold at the surface, 0.3 ± 0.1 ng Au/l, decreased with depth, and remained fairly constant at 0.1 ± 0.05 ng Au/l from 50 to 1000 m (Fig. 6-15). The particulate gold concentrations followed the trend of the ionic gold in the near surface water, but were rather erratic with depth. The amount of particulate matter was very low, 0.4 ± 0.1 mg/l.

A comparison of samples filtered at sea with those filtered in the laboratory after acidified storage is shown in Fig. 6-16. The particulate gold concentrations are generally higher for stored samples and more erratic. The same was true of ionic gold concentrations (Fig. 6-17). While total gold concentrations are not seriously affected by acidified storage, samples must be treated while fresh in order to draw valid conclusions about their particulate or ionic character.

Station GA-2 on ACONA Cruise 064 was occupied to check the effect of the sampling bottle on the sample and also to collect water used to determine the precision of the pH measurement. The pH was determined following the method of Strickland and Parsons (1965). The pH of the 20 m water at GA-2 was 8.18 ± 0.01.

Ten liters of acidified sea water, which had been passed through anion exchange columns, were spiked with auric chloride thereby increasing the gold content to 4.8 ug Au/l. The pH was adjusted to about 8 with NaOH and one liter of water was removed as a control. The remainder was used in an experiment to check for adsorption and exchange of water in a closed sample bottle. A PVC sampling bottle was completely filled

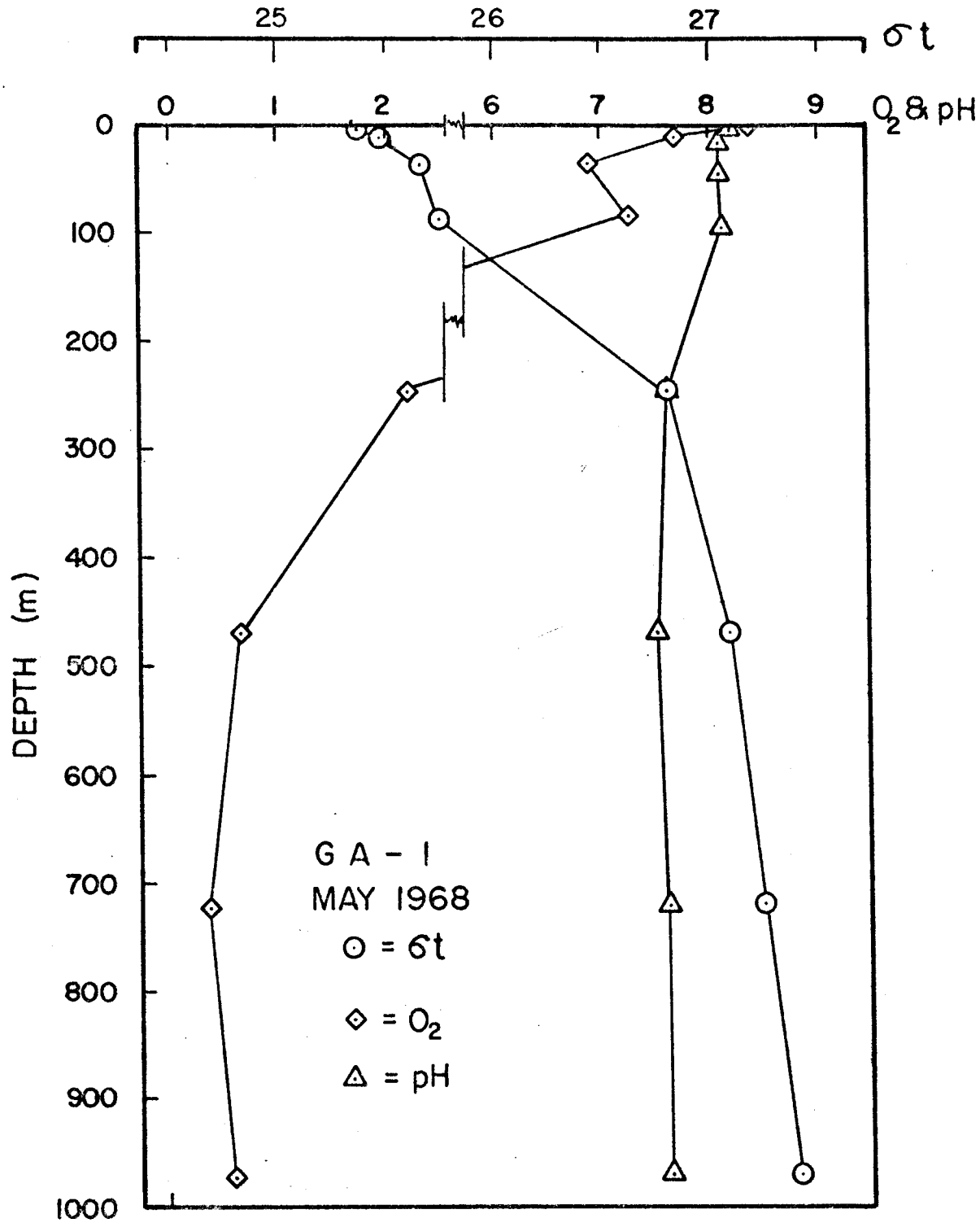

Fig. 6-14 Vertical distribution of σ_t, O_2 and pH for Gulf of Alaska station GA-1, May 1968.

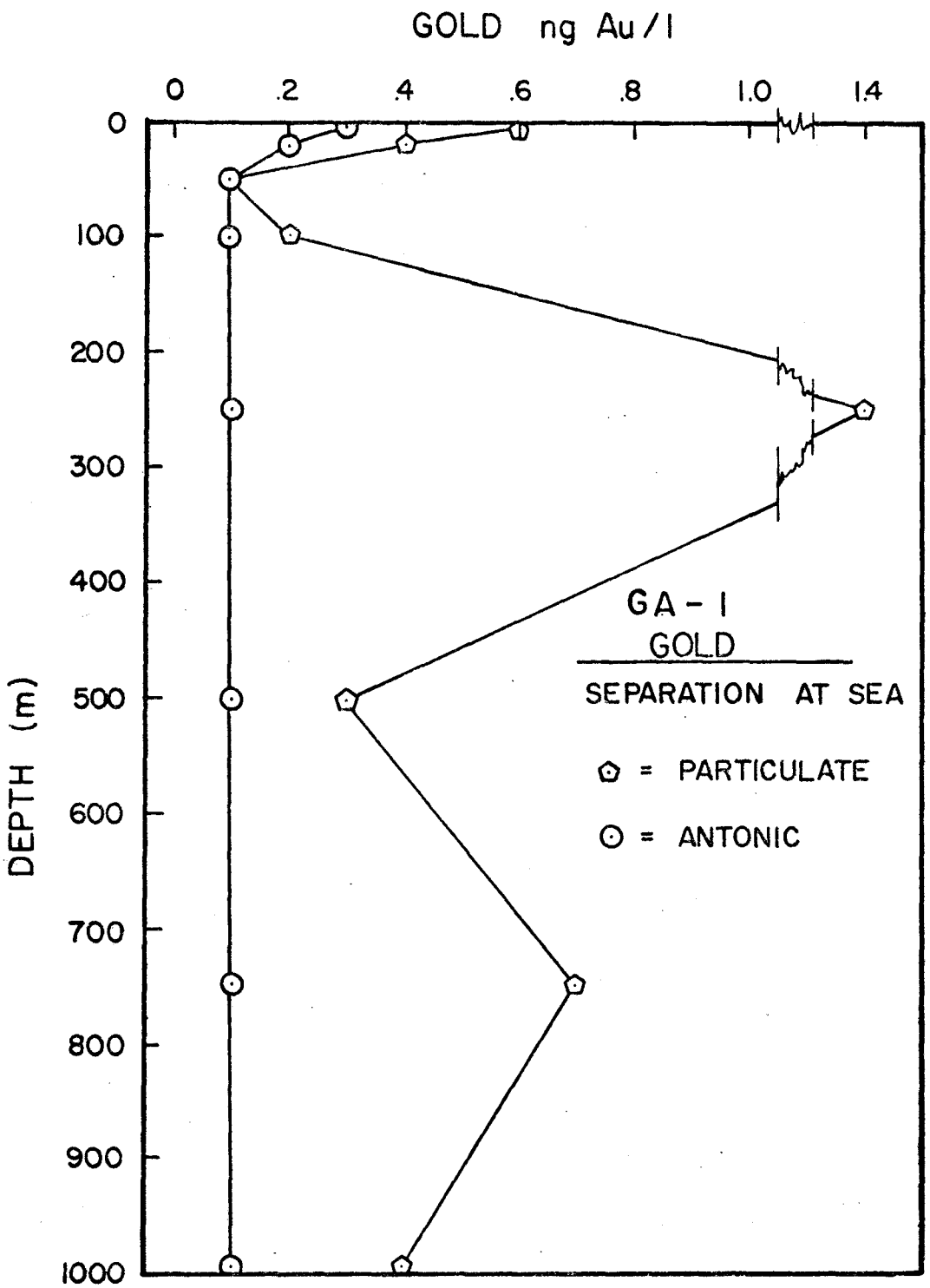

Fig. 6-15 Vertical distribution of anionic and particulate gold at Gulf of Alaska station GA-1 May, 1968.

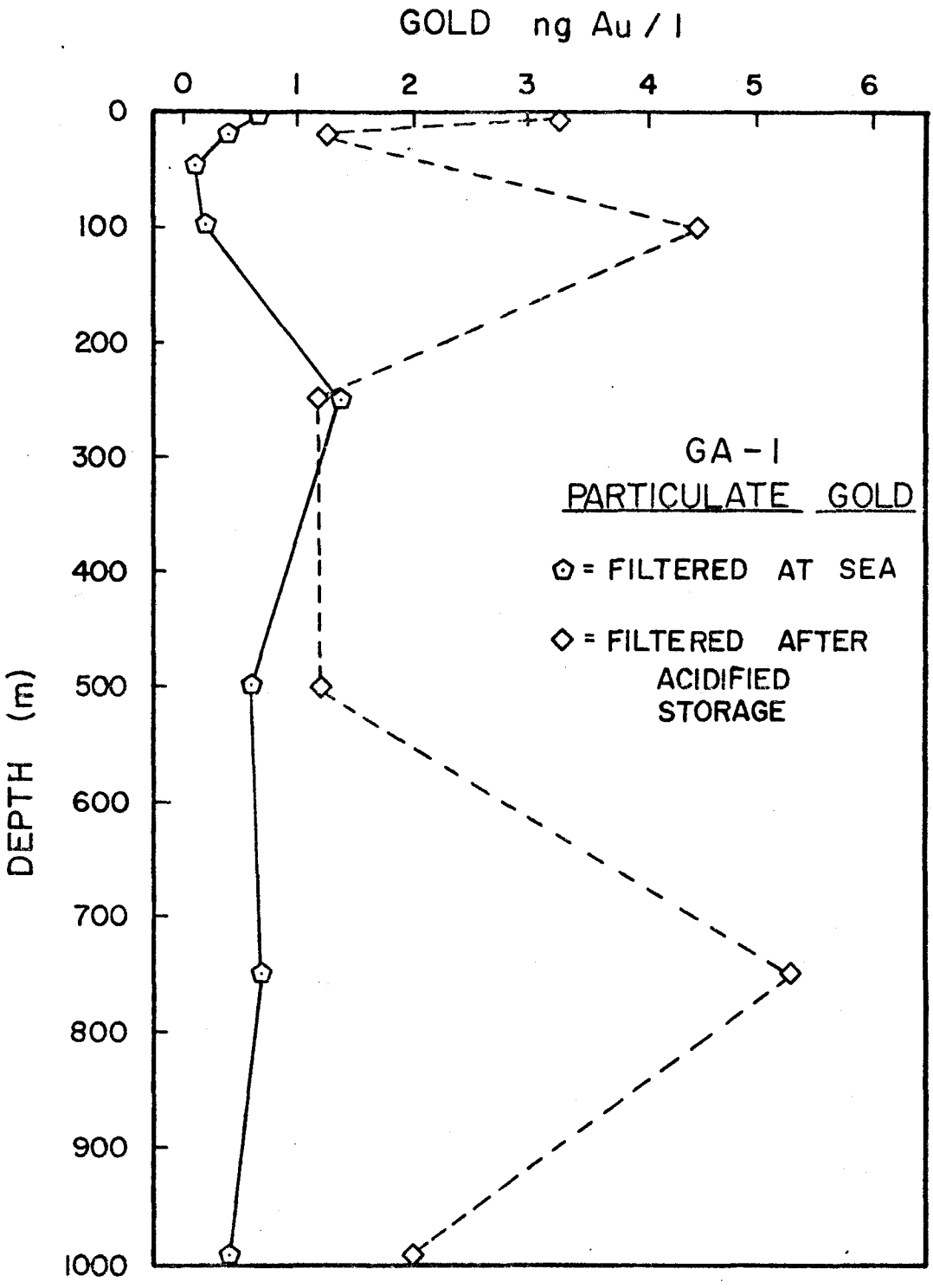

Fig. 6-16 Comparison of data for particulate gold for GA-1 for samples filtered at sea and filtered after a three month acidified storage.

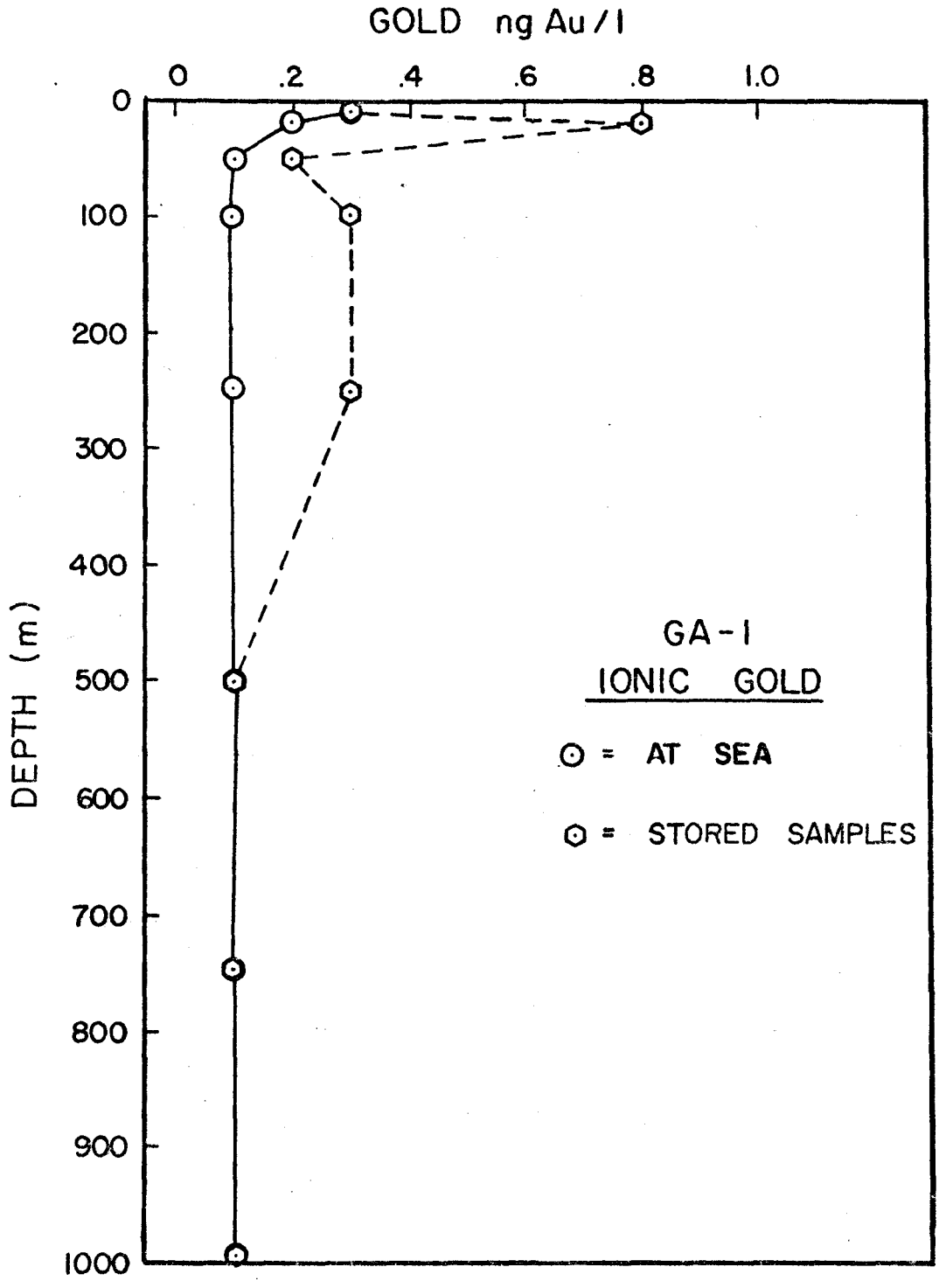

Fig. 6-17 Comparison of anionic gold profiles for samples passed through ion exchange columns at sea, and those stored for three months before ion exchange treatment.

and lowered to 30 m. The salinity of the control water and that which went down to 30 m and back were identical having a value of 30.60 °/₀₀. The water in the bottle was then treated as a regular sample. One liter was acidified (No. 1, pH = 1.5) and passed through an anion exchange resin column as was the control (No. 3, pH = 8). A second liter of the solution from the sample bottle was acidified (No. 2, pH = 1.5) and stored for three months before being passed through the resin column. The gold collected by the resin columns was as follows:

Sample No.	1	2	3
pH	1.5	1.5	8.0
µg Au/l	3.2	2.8	2.2

The ionic gold in the stored sample was a little lower than No. 1, but the difference in the two values is not greater than the analytical error. The effect of acidification can be seen from the lower ionic gold value of No. 3. The water surrounding the experimental bottle had a salinity of about 31.65 °/₀₀.

East Pacific Ocean and Caribbean Sea

Sea water samples from the east Pacific Ocean and Caribbean Sea were analyzed for total gold content. The results are given in Table 6-1 and the individual values of the replicates are presented in the Appendix. Some of the scatter in the results can be explained by experimental error which is on the order of 60% for the lowest values. However, much of the difference is real and probably a result of the heterogeneous nature of gold distribution in the ocean. Haber (1927) described this as a

Table 6-1. Station Data for GEOSECS Station

GEOSECS Guadalupe Is., E. Pacific - Lat. 28°29'N - Long. 121°38'W

Depth m	Total Gold	
	Non-Acidified ng Au/l	Acidified ng Au/l
50	2.3	4.7
450	25.1 ± 3.3(2)	2.3
650		10.8 ± 2.6(3)
1500	1.7	1.3
3500	1.6	2.4

Interlaboratory Comparison Study - Lat. 28°13'N - Long. 121°42'W

Sample No.	
1-5	2.0
1-14	7.3 ± 1.6(2)
1-75	2.2 ± 1.3(7)

Mixed Deep Sea Water from Caribbean Sea (East Cayman Basin
Venezuelan Basin
Columbian Basin)

Sample No.	
3-16	1.2
3-47	4.2
3-70	2.8

"clumping" effect and attributed it to colloidal gold and gold associated with biological and inorganic particulate matter. A plot of the GEOSECS samples furnished by D. E. Robertson is given in Fig. 6-18. The gold concentrations for the deep water are uniformly low, on the order of 1 to 2 ng Au/l. High values are seen at intermediate depths. The average for the acidified samples was 4.3 ng Au/l with a range of 1.3-10.8. The average for the unacidified samples was 7.7 ng Au/l with a range of 1.7 - 25.0 ng Au/l.

CHEMICAL FORMS AND ASSOCIATIONS OF GOLD IN SEA WATER

Gastineau Channel

Surface water was obtained from the Gastineau Channel in August, 1968, from mid-channel near the Institute of Marine Science station at Douglas. The sample was divided into four portions and treated to determine the distribution of various forms of gold in sea water and the effect of acidification on this proportionation. The scheme and results are shown in Table 6-2. The acid persulfate treatment was performed by refluxing one liter portions of seawater with 10 ml 0.1 $\underline{N}$ $K_2S_2O_8$ and 10 ml 0.4 $\underline{N}$ HCl for 5 min.

A value of 5.8 $\pm$ 1.4 ng Au/l was determined for the total gold concentration by the freeze-dry method of drying sea water. The amount of gold retained on 0.45 μ filters (samples 2 and 3) and on anion exchange resin (sample 3 and 4) was about 10% and 20% of the total gold, respectively. Only a trace of gold was retained on a 0.01 μ filter (sample 3) which indicates that if gold is in a colloidal form, the size range must be 1-10 μ. The high particulate gold value found in sample

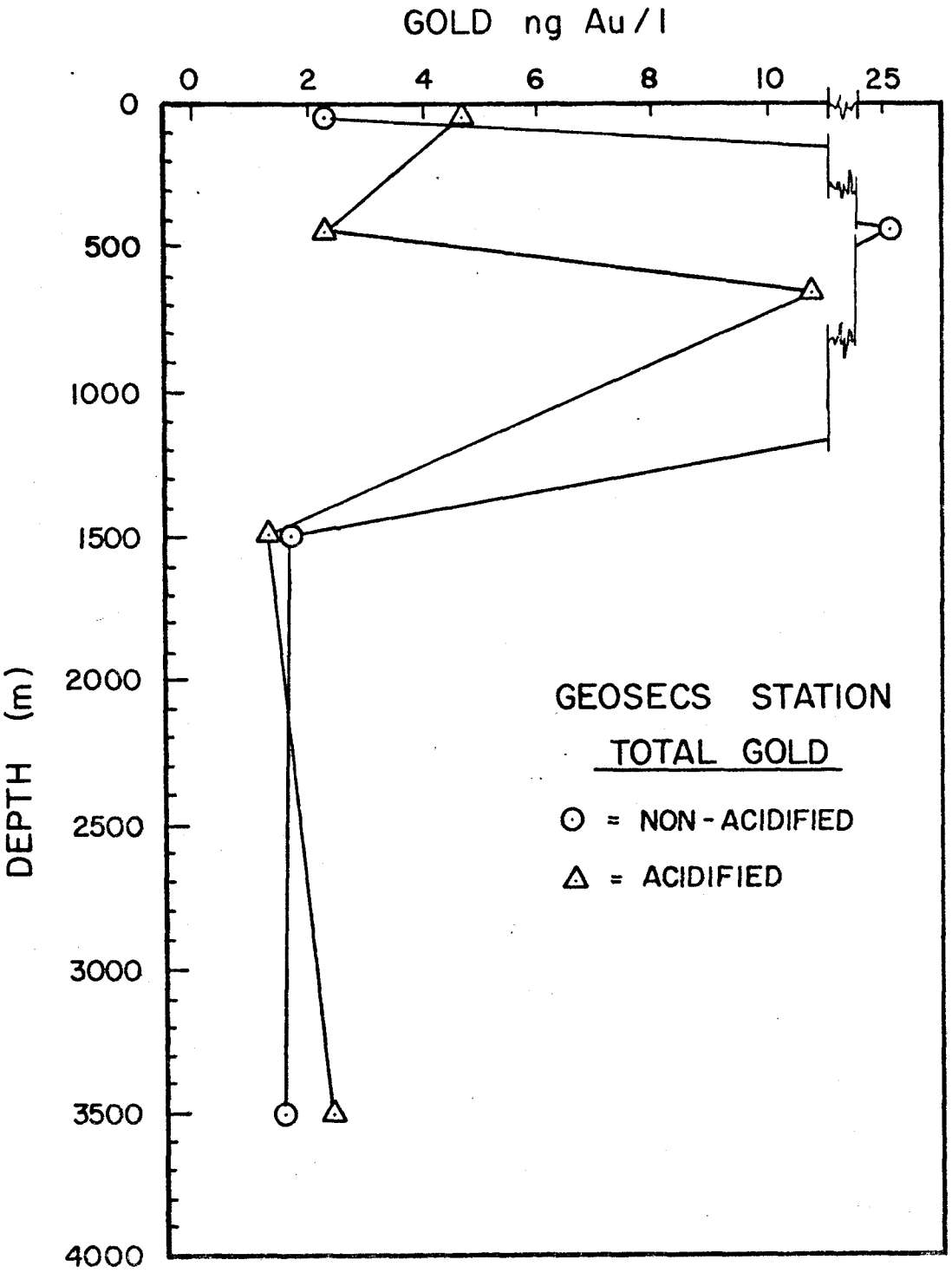

Fig. 6-18 Profile of total gold in GEOSECS station 1969 for acidified and non-acidified samples. Station located near Guadalupe Island at 28° 29'N Lat., 121°38'W Long.

Table 6-2. Gastineau Channel surface water treatment scheme used to determine the distribution of gold within a sample.

Lat. 58°16.7'N - Long. 134°23'W - August, 1968 - Gold in Gastineau Channel surface water = 5.8 ± 1.4 ng Au/1, 5.6 mg particulate matter/1.

Sample 1	ng Au/1	Sample 2	ng Au/1	Sample 3	ng Au/1	Sample 4	ng Au/1
Acid persulfate		Filter 0.45 μ 3.2 mg P.M./1	0.5	Filter 0.45 μ 3.8 mg P.M./1	0.5	Acidification	
						Filter 0.45 μ	1.8
Filter 0.45 μ 2.2 mg P.M./1	0.00	Acid persulfate reflux		Acidification 0.01 μ trace			
Anion exchange resin	4.9 ± 0.6(2)	Anion exchange resin	4.4 ± 0.8(2)	Anion exchange resin	1.4 ± 1.0	Anion exchange resin	0.8 ± 0.2(2)
		Gold in effluent	0.6 ± 0.2				
	TOTAL GOLD				PARTICULATE + IONIC GOLD		
	4.9 ± 0.6		5.5 ± 1.3		2.1 ± 1.3		2.6 ± 0.9

4 may be the result of ionic gold adsorbed on the filter from an acidified sample, as suggested by tracer experiments (Chapter II). The values for total gold content in samples 1 and 2 correspond reasonably well with the value obtained from the freeze-dry sample.

Northeast Pacific Ocean

Most of the samples analyzed thus far indicate that while ionic and particulate gold concentrations vary from near zero to as much as half of the total gold content, the average of their combined concentrations only account for 20% of the total gold.

A cruise into the Gulf of Alaska was made aboard the U.S.C. & G.S. RAINIER in April 1970 (Fig. 6-5). A scheme was designed to define more clearly the associations and states of gold in seawater. The scheme (Fig. 6-19) consisted of a partially closed system in which surface water samples of ten liters each were filtered through Millipore in-line filters and then run through an ion exchange column. The columns were prepared in the laboratory by stacking six 2/5 dram polyethylene capsules. The top three capsules contained strong anion exchange resin AG-1-X8 and the lower three contained a strong cation resin AG-50-X8. Both were 100-200 mesh size. The capsules were held together by spot welds and then wrapped in Parafilm to allow a vacuum to be maintained. Numerous pinholes in the bottom of each capsule allowed the water to pass through into a 20 l Pyrex carboy. A vacuum was applied and a flow rate of 4-5 ml/min was maintained.

A 30 ml water sample was drawn before and after the filtration-ion exchange process. The processed water was extracted with 200 ml of

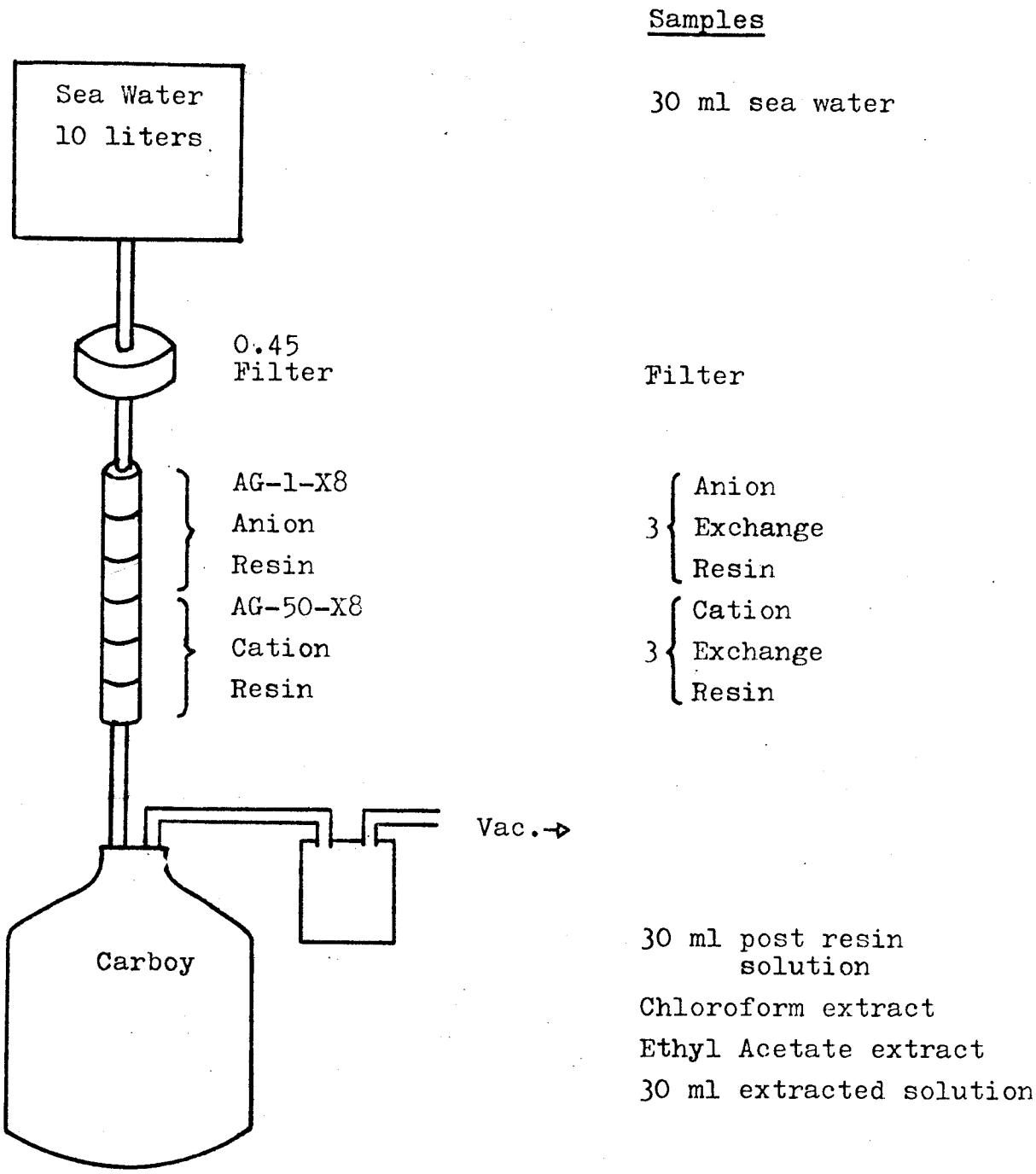

Fig. 6-19 Scheme for sampling northeast Pacific Ocean water to determine the distribution of gold within the sample.

redistilled chloroform and then with 200 ml of redistilled ethyl acetate to test for a possible association of gold with dissolved organic matter extractable by these solvents. The mixture of the ethyl acetate and the chloroform (which remained in the seawater after the first extraction) was more dense than the seawater so that it was possible to pipette the organic solvents of both extractions from the bottom of the carboy. A water sample was also taken from the extracted seawater. Six runs were made with the even numbered runs being acidified. The question of possible filtration by the ion exchange resin was tested by reversing the order of the types of resin in runs 5 and 6.

The samples were returned to the laboratory for drying and packaging for neutron activation analysis. The results are shown in Table 6-3. The data are not as consistent as was desired, however several conclusions can be reached. There appears to be a loss of gold due to absorption on the container walls in the non-acidified samples and the concentration of anionic gold generally increased with acidification. The anion exchange resin is more efficient at pH 1 than at pH 8 and the ionic form of gold is certainly altered also.

The cation resin was nearly devoid of gold as expected. The filtering effect of the resin seems to be minimal and the 0.1 ng Au/l value for the second cation capsule in station 6 was probably erroneous.

CONCLUSIONS

The concentration of gold in sea water is variable (1-25 ng Au/l)

Station / Description	P-1	P-2	P-3	P-4		P-5	P-6
Location:							
Lat.	59°00'N	52°43'N	54°23'N	56°45'N		54°46'N	54°00'N
Long.	138°00'W	141°57'W	149°44'W	153°00'W		155°06'W	161°54'W
Acid Treatment	Non-acidified ng Au/l	acidified ng Au/l	Non-acidified ng Au/l	acidified ng Au/l		Non-acidified ng Au/l	acidified ng Au/l
Sea Water (Total)	0.92		1.62	3.24		0.65	2.23
Filter	0.04	0.08	0.52	0.45		0.40	0.51
Anion Resin	0.03	1.19	0.19	0.15	Cation Resin	0.01	0.00
	0.00	0.35	0.13	0.00		0.00	0.10
	0.00	0.02	0.00	0.00		0.00	0.00
Σ	0.03	2.36	0.32	0.15		0.01	0.10
Cation Resin	0.00	0.00	0.00	0.00	Anion Resin	0.02	1.67
	0.00	0.00	0.00	0.00		0.00	0.02
	0.00	0.00	0.00	0.00		0.00	0.04
Σ	0.00	0.00	0.00	0.00		0.02	1.73
Sea Water (After Resin Treatment)	0.24		1.63	1.22		1.08	1.14
Chloroform	0.00		0.01	0.00			0.00
Ethyl Acetate	0.01	0.00	0.00	0.00			0.00
Sea Water (After Extraction)	(1.80)	0.99	0.85	0.40			1.42
Particulate Matter mg/l	1.0	0.2	0.2	0.6		0.2	0.3

especially in surface and near surface waters. Bottom waters in the open ocean tend to be low in gold (1-3 ng Au/l) with more uniformity. Even waters in the vicinity of terrestrial placer gold deposits are not exceptionally high in gold. Natural processes of adsorption and scavenging prevent gold concentrations from attaining the solubility observed in the laboratory. The gold associated with particulate matter and that which is retained on strong anion exchange resin are on the order of 10-20% each. Approximately 50% of the gold is in a non-ionic form and is less than 0.01 μ in size. There is little gold associated with dissolved organic matter extractable in the solvents used. A more rigorous pursuit of this problem using multiple techniques as well other solvents is warranted before organic associations with gold can be clarified. The great difference in resin exchangeable gold before and after oxidation with persulfuric acid is a strong indication of the possible importance of organic association with gold in most sea water samples.

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CHAPTER VII

SUMMARY

The value man has placed on gold and the stature given it as the foundation of our monetary system has inspired the geochemical study of this metal for years. Early measurements of gold in sea water were erroneously high and caused numerous attempts to extract the metal from the oceans. An extensive study by Fritz Haber and his co-workers put the average content of gold in sea water at 4 ng/l with a range of < 1 to ca 60 ng Au/l. Later analyses by a number of investigators generally confirmed the findings of Haber even though some reported substantially higher values. Gold cannot be economically extracted from sea water by any method presently available. This study has attempted to characterize the state of gold in sea water and to determine the processes by which gold is dissolved, transported, and precipitated in sea water in order to better understand the chemistries of this element in the environment.

Radioactive gold tracers were used to study the behavior of the metal in artificial sea water. Distinction was made between particulate and soluble gold as defined by 0.45 μ filtration or centrifugation at 2500 rpm for 20 min in a clinical centrifuge. The reproducibility of particulate gold determinations was erratic. A strong anion exchange resin retained both gold +1 and gold +3, although gold +3 was more strongly retained.

Dialysis of sea water equilibrated with gold showed that some of the gold is present in a form larger than the 24 A porosity of the dialysis bag. Electrophoresis confirmed the anionic nature of ionic gold.

Neutron activation analyses (NAA) methods were devised to determine the total amount of gold in various kinds of appropriate samples. The method was used to determine the gold associated with particulate matter,

in ionic forms, extractable in organic solvents, sediments and sea water.

The solubility of gold in sea water was determined by allowing solutions initially saturated with gold and gold-free to equilibrate with radioactive ^{195}Au. Equilibrium was reached in about four months at a concentration of about 4 µg Au/l.

Gold was determined in the sediment of Gold Creek near Juneau, Alaska and in Gastineau Channel into which Gold Creek flows. Gold was associated with 4 ϕ or smaller size. The size of the sediment fraction with which gold was predominantly associated decreased with distance from the source. The very fine sediment may have contained gold adsorbed on clays as suggested by laboratory studies. Clays adsorbed gold III rapidly, then released it upon reduction to gold I. Gold was then readsorbed slowly, probably as colloidal gold produced by reduction of gold I.

Water and sediment samples adjacent to gold-bearing areas in southeastern Alaska were analyzed for gold as were open ocean samples and samples from an anoxic fjord. The gold content of the sediment ranged from 0.02 to 0.10 µg Au/g sed. with values over 1 µg Au/g sed. in some sediment size splits. Water overlying these sediments contained gold concentrations up to 11 ng/l, but were usually from 3-5 ng/l. Ionic gold and gold associated with particulate matter was ca 10-20% of the total. Oxidation of the water samples allowed nearly quantitative recovery of gold on strong anion exchange resin.

Open ocean samples showed generally higher values in upper waters, erratic concentrations at intermediate depths corresponding to the

oxygen minimum, and low, nearly uniform concentrations in the deep water. No noticeable deviation from open ocean concentrations was noted for the gold in the waters of an anoxic basin sampled. Gold in sea water is present in quantities nearly three orders of magnitude below concentrations attainable in the laboratory, principally in non-ionic, non-particulate forms.

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